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Synthesis of Bio-Based Epoxy Resins

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1.1 Introduction

The term "epoxy resin" is understood to mean compounds containing at least one active epoxy group in their structure and which are capable of forming a cross-linked three-dimensional structure in the curing process involving these groups. Naturally, epoxy rings are found only in vernonia oil. However, epoxy functionality can be easily introduced into the compound structure, even by the oxidation of unsaturated bonds to oxirane rings. This is a typical method of obtaining cycloaliphatic resins, applied on a large scale in electronics to encapsulate electronic systems. The second method is the use of epichlorohydrin, which is commonly applied to prepare epoxy compounds via the reaction with polyalcohols or polyphenols. Epichlorohydrin together with bisphenols (mainly bisphenol A or F, and S) are the main raw materials used in industrial methods for the synthesis of epoxy resins most often produced and used on a large scale. All these compounds are of petrochemical origin. There are three main reasons for the search of new raw materials of natural origin for the synthesis of epoxy resins. The first is the need to replace petrochemical raw materials. The volatility of oil and gas prices and their strong connections with the changing political situation in various regions of the world, as well as the inevitable prospect of imminent exhaustion of their sources, and ecological considerations are the main reasons for the search of alternative sources of raw materials. Moreover, potential toxicological and endocrine disrupting properties of bisphenol A are discussed and emphasized, especially in recent years. The second reason is the need to solve the problem of annually increasing amount of postconsumer plastic waste. Epoxy resins belong to the category of polymeric materials practically not biodegradable. The application of bio-based raw materials can enable and facilitate their decomposition under the influence of biological factors. Epoxy resins are widely used as coating materials in products intended for contact with food or even storage of food (e.g. can-coating or paints for securing ship hold walls). Therefore, the third reason is the need to limit the penetration of harmful

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substances such as bisphenol A into food from the coating material, preferably by eliminating them already at the stage of synthesis.

While searching for new bio-based resources for the synthesis of epoxy resins, particularly bisphenol substitutes, the crucial issue must be remembered. One of the most important challenges is to provide new bio-based resins with comparable performance properties to the currently manufactured and applied petrochemical-based commercial products, i.e. primarily high mechanical strength, thermal stability, and chemical resistance. The mentioned properties are characteristic of the resins based on bisphenol A (or other bisphenols), thanks to which these materials are produced on a large scale for many applications. Therefore, this chapter presents the most promising raw materials whose structure can provide the desired final properties of the epoxy system after cross-linking. At the same time, they must be raw materials easily available in large quantities from renewable sources, nontoxic and cheap to obtain and in preparation.

1.2 Plant Oil Bio-Based Epoxy Resins

Vegetable oils, as a material of natural origin and from renewable sources, are the subject of numerous studies aimed at their application for the synthesis or modification of various polymers [1]. Soybean, castor, linseed, rapeseed, sunflower, cotton, peanut, and palm oils are primarily used on a larger scale depending on the type of oil produced in a given region [2]. From the chemical point of view, plant-based oils are a mixture of esters derived from glycerol and free fatty acids, mainly unsaturated acids (primarily oleic, linoleic, linolenic, ricinoleic, and erucic acids) and in a small amount of saturated acids (stearic and palmitic acids) (Figure 1.1), depending on the type of oil.

When choosing vegetable oil for use in the synthesis of polymers, first of all, its structure should be taken into account: the presence of unsaturated bonds and possibly other functional groups (e.g. hydroxyl in castor oil or epoxy in vernonia oil), the amount of unsaturated bonds present in the molecule (referred as the oil functionality), and chain length alkyl derived from fatty acids (Table 1.1).

The functionality of oils (understood as the content of unsaturated bonds) primarily determines the cross-linking density of oil-based chemosetting polymers or polymers obtained by free radical polymerization as well as oil-modified polymeric materials. In turn, the final polymer properties such as mechanical strength, thermal stability, and chemical resistance strongly depend on the

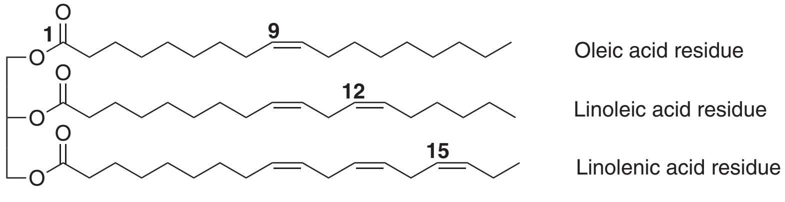


Figure 1.1 Schematic structure of triglycerides.

Table 1.1 The content of various fatty acids in selected vegetable oils.

Fatty acid	Vegetable oil, content of individual acids (wt%)					
	Soybean	Rapeseed	Linseed	Sunflower	Castor	Palm
Palmitic	12	4	5	6	1.5	39
Stearic	4	2	4	4	0.5	5
Oleic	24	56	22	42	5	45
Linoleic	53	26	17	47	4	9
Linolenic	7	10	52	1	0.5	—
Castor	—	—	—	—	87.5	—
Other	—	2	—	—	—	2
Functionality	4.6	3.8	6.6	4.6	2.8	1.8

cross-linking density. The elasticity of the polymers with the addition of vegetable oil or based on them depends on the length of the alkyl chains in the oil molecule derived from fatty acids.

Vegetable oils can be easily and efficiently converted into epoxy derivatives by oxidizing unsaturated bonds present in fatty acid residues. Several methods of double bond oxidation in triglyceride molecules are known and commonly used [3]: the method based on the Prilezhaev reaction, the radical oxidation, the Wacker-type oxidation, dihydroxylation of oils and fats, and enzyme–catalyst oxidation. The Prilezhaev reaction is the most often used method for natural oil epoxidation, commonly applied in the industry. In this method, the process of epoxidation of natural fatty acids and triglycerols is carried out in the system consisting of hydrogen peroxide, an aliphatic carboxylic acid, and an acidic catalyst. The organic peracid formed *in situ* by the reaction of acid with hydrogen peroxide is the real oxidizing agent in this method (Figure 1.2).

Carboxylic acids with one to seven carbon atoms are the most commonly used (in practice, mainly acetic acid). Inorganic or organic acids and their salts, as well as acidic esters, can be used as catalysts; however, sulfuric and phosphoric acid are the most often used in industrial practice. A promising method is oxidation in the presence of enzymes [4], heteropolyacids [5], and even ion exchange resins [6] as catalysts. The most commonly used oxidizing agent is hydrogen peroxide in the form of solution with a concentration of 35–90% (usually 50%). Epoxidation of plant oils in ionic liquids, as well as in supercritical carbon dioxide, is also described [7].

The earliest epoxidized esters of higher fatty acids have found wide applications as both plasticizers and stabilizers for thermoplastics, mostly poly(vinyl chloride), poly(vinylidene chloride), their copolymers, and poly(vinyl acetate) and chlorinated rubber [8, 9]. Epoxidized fatty acids containing oleic acid are used as a valuable intermediate in the production of lubricants and textile oils [10, 11]. It seems that epoxidized vegetable oils could also be used as hydraulic liquids [12]. However, primarily, they can also act as reactive diluents of bisphenol-based epoxy resins [13], which are usually highly viscous. They have oxirane groups, although

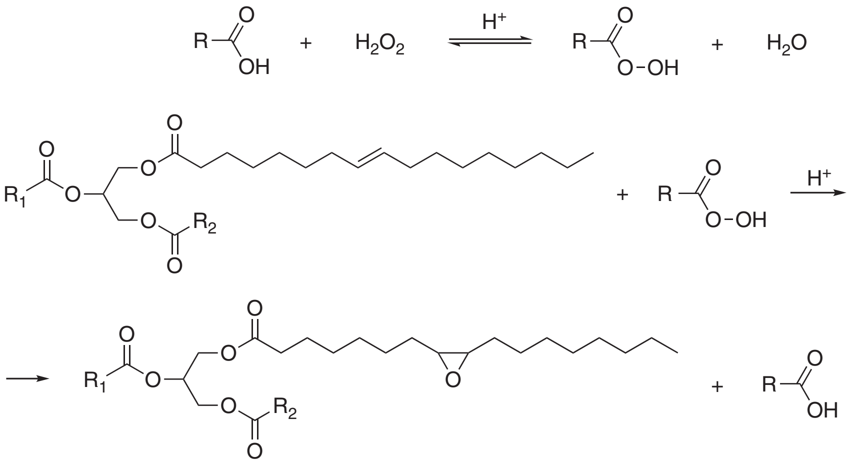
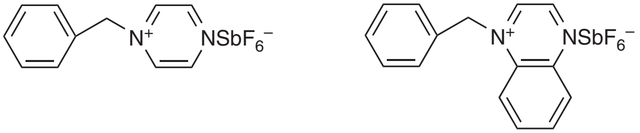


Figure 1.2 The reaction of triglyceride epoxidation with organic peracids.

less reactive because of their central location in triglyceride chains (compared to terminal glycidyl groups), but also capable of reacting with polyamines or carboxylic anhydrides. By building into the structure of the cured resin in the process of co-cross-linking with it, they affect its final properties – improving flexibility and impact strength. In this way, embedded triglycerides not only facilitate the processing of resins with high intrinsic viscosity but also allow limiting their typical disadvantages (high brittleness, low impact strength, and flexibility) resulting from the rigid structure they owe because of the structure of bisphenols [14].

However, the first, logically implied possibility of use of epoxidized vegetable oils is their application as stand-alone materials: the networks cross-linked with bifunctional compounds such as dicarboxylic acids or aliphatic and aromatic diamines, which are typically used as hardeners for the epoxy resins. Because of the content of more than one epoxy group in the molecule, epoxidized triglycerides may, according to the generally accepted definition, be treated as epoxy resins. However, curing of, e.g. epoxidized soybean oil [15] or vernonia oil (natural epoxidized oil mainly obtained from plant *Vernonia galamensis*), dicarboxylic acids [16] resulted in obtaining only soft elastomers. Materials with higher mechanical strength are synthesized by reacting epoxidized oils first with polyhydric alcohols (e.g. resorcinol) and phenols or bisphenols and then cross-linking the obtained modified oil with partially reacted epoxidized rings [17]. Finally, curing by photopolymerization or polymerization with latent initiators allows to obtain from modified vegetable oils, without the addition of the bisphenol-based or cycloaliphatic resins, coating materials with satisfactory mechanical properties. It was found [18] that the properties of hardened vegetable oils also depend on the type of used thermal latent initiator. The properties of epoxidized castor oil cross-linked with *N*-benzylpyrazine (BPH) and *N*-benzylquinoxaline (BQH) were studied (Figure 1.3).

It was found that materials characterized by a higher glass transition temperature, a higher value of the coefficient of thermal expansion, and greater



BPH BQH

Figure 1.3 Chemical structure of cationic photoinitiators.

thermal stability are obtained using BPH as a photoinitiator. Nevertheless, the composition cross-linked with BQH is characterized by better mechanical properties. Most likely, the better final properties result from the higher cross-linking density of cured with BPH composition. Anhydrides of various carboxylic acids are used to cure epoxidized linseed oil [19], and cross-linking reactions are catalyzed by various tertiary amines and imidazoles. The materials obtained with phthalic anhydride and methylendomethylenetetrahydrophthalic anhydride hardeners exhibit a lower cross-linking density than those obtained with *cis*-1,2,3,6-tetrahydrophthalic anhydride. It was found that a greater degree of oil–anhydride conversion and thus higher cross-linking density and greater rigidity of the cured material are obtained using imidazoles. The best properties are achieved for the composition cured with *cis*-1,2,3,6-tetrahydrophthalic anhydride as the hardener and 2-methylimidazole as the catalyst.

High-molecular-weight epoxies are a special group of very important epoxy resins commonly used as coating materials, especially for powder, can and coil coatings mainly in automotive industry. Theoretically, they can be obtained in the traditional way in the Taffy process with epichlorohydrin and bisphenol. However, even the use of a slight excess of epichlorohydrin does not provide high-molecular-weight solid resins. Therefore, industrially, they are synthesized from low or moderate molecular weight epoxy resins and bisphenol A by the epoxy fusion process. It is the method of polyaddition carried out in bulk, in the molten state of reagents, and without the use of solvents. In this way, it is possible to obtain resins with a softening temperature of 100–150 °C, characterized by an epoxy value of 0.020–0.150 mol/100 g, and an average molecular weight of 1.5–10 thousands of Daltons. The application of epoxidized vegetable oils in place of low/medium molar mass resins, as well as hydroxylated oils in place of bisphenols, in the epoxy fusion process with bisphenol A (BPA) or BPA-based epoxy resin was proposed [20, 21]. Hydroxylated oils are obtained from epoxidized oils in the reaction of opening of oxirane rings using diols and the most often glycols. Depending on the type of starting oil, catalyst used, and reaction time, the products of the epoxy fusion process using modified oils (Figure 1.4) contain a large amount of hydroxyl groups (hydroxyl value 120–160 mg KOH/g), some free epoxy groups (epoxy value 0.050–0.150 mol/100 g), and are characterized by weight-average molecular weight even above 30 000 g/mol.

Therefore, for the cross-linking of these products, diisocyanates or blocked diisocyanates can be applied (Figure 1.5).

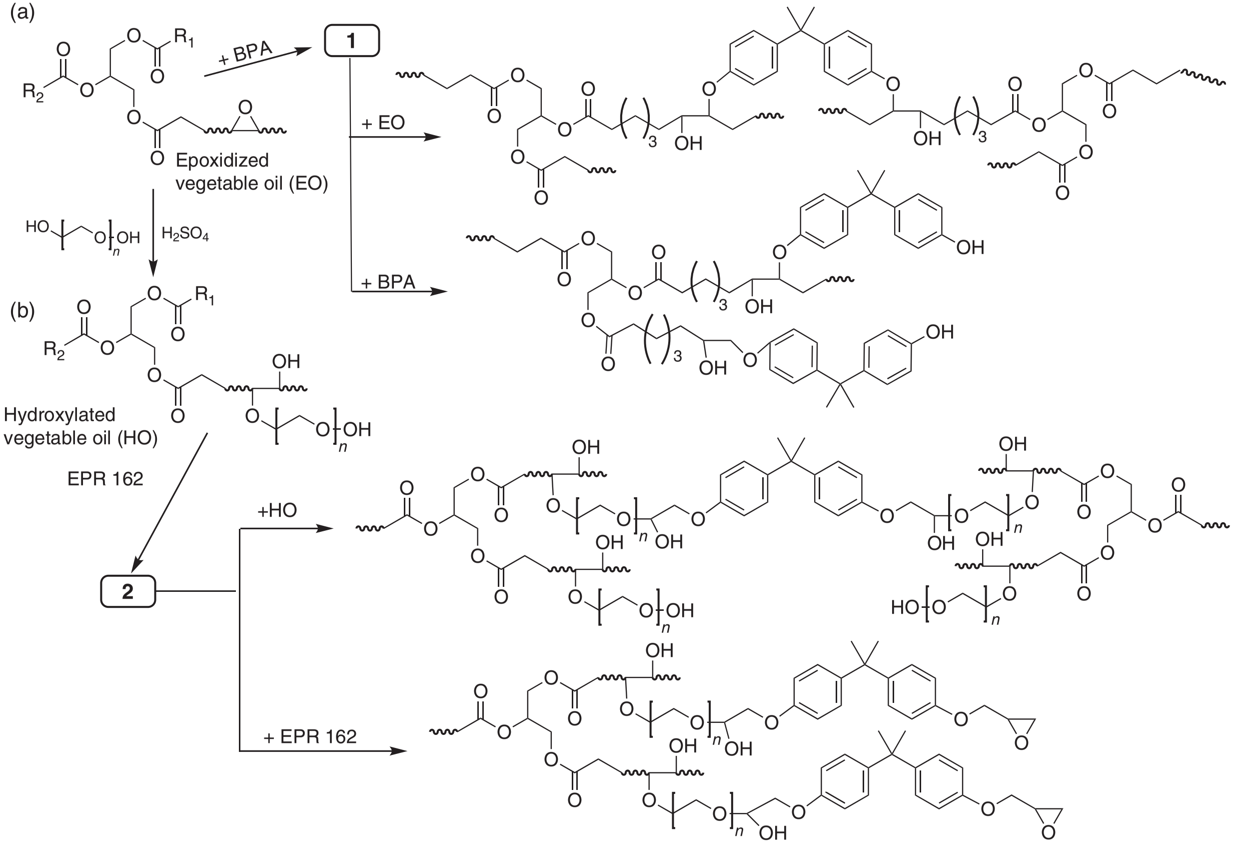


Figure 1.4 The synthesis of high-molecular-weight epoxy resins based on modified vegetable oil: (a) epoxidized or (b) hydroxylated soybean oil.

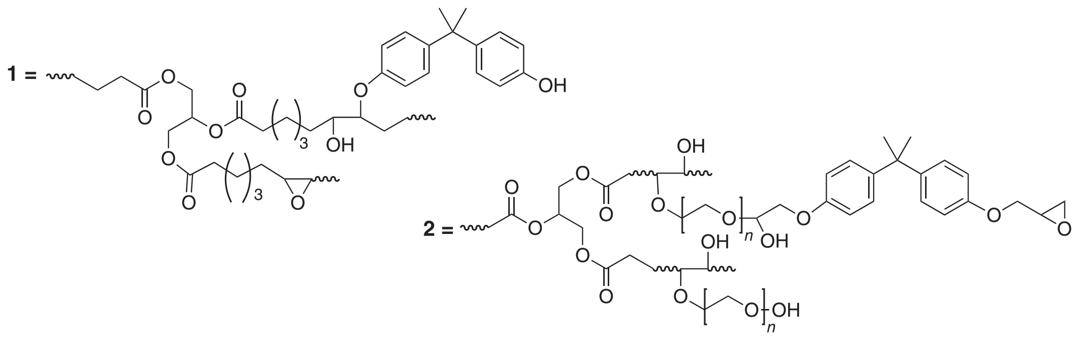


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Figure 1.4 (*Continued*)

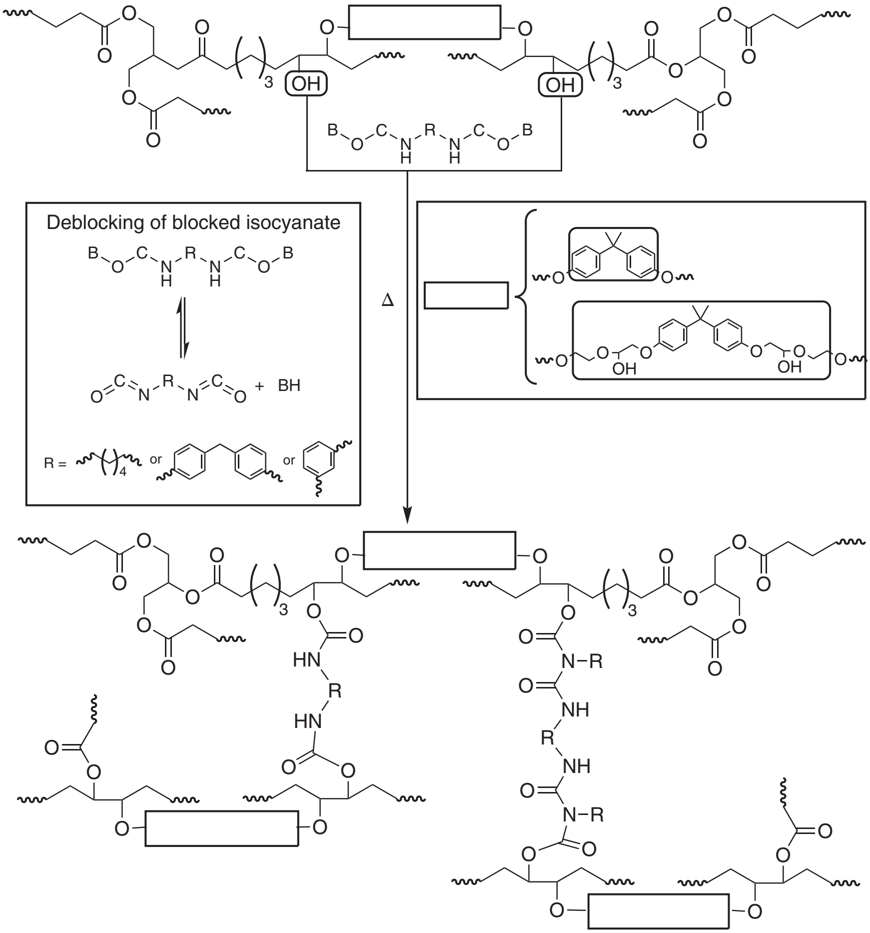


Figure 1.5 Cross-linking reactions of epoxy fusion process products.

The resins cross-linked with polyisocyanates are characterized by differential mechanical properties, which depend on the type of used isocyanate, and are higher than the one of the low-molecular-weight bisphenol A-based resin crosslinked with methyl-tetrahydrophthalic anhydride, however lower while cured with isophoronediamine [22]. Moreover, the presence of epoxy groups in the polyaddition products can be used to obtain two-layer materials [23], in which one layer is cured with polyamine epoxy resin and the other is a polyaddition product cross-linked with diisocyanate. The reaction of the amine hardener with the free epoxy groups that are present within the polyaddition product ensures a very good interlayer bonding.

Because of the usually unsatisfactory properties of the oils cured with amines or acid anhydrides, epoxidized vegetable oils began to be used as one of the components of epoxy compositions [24]. The compositions consisting of epoxidized esters of higher fatty acids obtained by the transesterification of various vegetable oils and natural or hydrocarbon resin acids can be used as an ingredient in, among others, epoxy adhesives with reduced crystallization tendency [25]. Compositions of modified vegetable oils with epoxy resins based on various bisphenols can generally be prepared via two methods. One of them is the homogenization of the components of the composition and their simultaneous co-cross-linking. In this way, compositions of bisphenol F diglycidyl ether with epoxidized linseed oil are prepared [26] and cured with methyltetrahydrophthalic anhydride in the presence of 1-methylimidazole or polyoxypropylenetriamine [27]. It turned out that with an increase in the content of epoxidized linseed oil in the anhydride-cured compositions, the storage modulus, glass transition temperature, and heat resistance under load decrease, while the impact strength measured by the Izod method does not change, but above 70 wt% of oil content increases the cross-linking density. In contrast, compositions cured with the use of amine are characterized by an almost fivefold increase in impact strength at the oil content of 30% by weight. Other discussed cured parameters change in the same way as in the case of anhydride cross-linked materials. In turn, comparison [28] of the properties of the composition with epoxidized linseed oil and soybean oil shows significant differences between the materials based on both oils. It was found that, due to the greater compatibility of linseed oil with the epoxy resin and better oil solubility in the resin (resulting from greater polarity and functionality and lower molecular weight), linseed oil does not tend to form a separate phase. However, the two-phase structure, observed in the case of epoxidized soybean oil, is responsible for improving the impact strength and fracture toughness of the epoxy resin composition. A decrease in cross-linking density is also observed in the compositions of 4,4′-tetraglycidyldiamino-diphenylmethane with epoxidized soybean oil cured with diaminodiphenylmethane [29]. Also in this case, besides the improvement in impact strength, as the effect of reducing the cross-linking density, a decrease in the heat resistance and the glass transition temperature is observed. Using the example of a bisphenol-based epoxy resin compositions with different contents of epoxidized castor [30] or soybean oil [31], cured with thermal latent initiator BPH, it was proven that the final properties of cross-linked materials are determined not only by the polarity, functionality, or structure of the used oil but also by its content, ensuring the optimal amount of flexible fragments embedded in the rigid epoxy resin structure, and the most favorable phase composition of the material.

Bisphenol-based epoxy resin compositions with modified vegetable oils might also be prepared in the two-step method. The first stage is the initial cross-linking of oil so that free functional groups capable of co-cross-linking with the epoxy resin remain in it. In this way, a prepolymer or, as it is called in some publications, a rubber is obtained from the modified oil. Only then, the prepared prepolymer is mixed in appropriate proportions with epoxy resin, and finally, the composition is cured. The cross-linked composition is characterized by a two-phase structure, analogous to that of epoxy resins modified with liquid acrylonitrile butadiene copolymers with reactive carboxyl or amine end groups and acrylic elastomers. The two-phase structure of the composition determines their postcuring properties. Using the two-step method, composition of diethylene epoxy resin with epoxidized soybean oil was prepared [32]. Initially, both the oil and then the composition with the epoxy resin were cross-linked with 2,4,6-*tri*(*N*,*N*-dimethylaminomethyl)phenol. The soybean prepolymer, cross-linked for 12–84 hours, is a highly viscous liquid that mixes well with the epoxy resin [33]. The formation of the two-phase structure of the cured composition was confirmed by DSC and DMA analyses. The adhesive joint prepared with the use of the tested composition shows a significant improvement in the impact strength and the strength. It has been found that the properties of the composition depend on both the content of soybean prepolymer and the time of its pre-cross-linking. The best results are obtained using the addition of 20 wt% of prepolimer pre-cross-linked for 60 hours. Compositions characterized by greater cross-linking density and mechanical strength than the networks with epoxidized soybean oil were obtained using methyl and allyl esters, synthesized by the transesterification of soybean oil [34]. The esters were epoxidated and then precured with *p*-aminocyclohexylmethane, which showed the highest reactivity to soybean oil derivatives among the tested polyamines. The curing conditions were selected in such a way that cross-linking of both esters and epoxidized oil, which was chosen for the comparison purposes, terminates at the gelation stage. The bisphenol-based epoxy resin compositions, with the content of prepolymers of 10–30 wt%, were cured using various polyamines, and their mechanical properties were compared with those of the samples of analogous composition but obtained via the one-step method. Generally, the mixed compositions with various soybean oil derivatives obtained by the two-stage method are characterized by the best strength parameters, definitely better than the networks synthesized only with epoxidized oil. In particular, the addition of epoxidized allyl ester increases the glass transition temperature and provides greater rigidity and mechanical strength of the composition.

Additionally [35], the process of cross-linking of the above-described materials with acid anhydride (the commercial product called Lindride LS 56V produced by Lindau Chemicals, USA) was studied. Based on the results of DSC and viscometric measurements, models describing the course of curing reactions have been developed, which might be applied in the industrial processing of the described compositions. The DMTA analysis showed [36] that the conservative modulus of elasticity and glass transition temperature increase with an increase in the content of epoxidized allyl ester in the case of anhydride cross-linking while decrease for polyamine-cured materials. Moreover, the value of the loss factor decreases in the case of anhydride cross-linking, but it is definitely higher for polyamine-cured compositions. That kind of formation of dynamic mechanical properties results from a greater degree of cross-linking of anhydride-cured compositions. The epoxidized palm oil was prepolymerized in a reaction with isophorone diamine [37]. The resulting palm oil derivatives were used as modifiers of a bisphenol A-based low molecular weight epoxy resin. The prepared compositions and the pure unmodified epoxy resin were cured with isophorone diamine. It was found that the palm oil derivatives led to a decrease in the mechanical strength of the resin, but on the other hand, they contributed to an increase in relative elongation at break and significant improvement (even twice) in impact strength of the cross-linked products. A two-phase structure of

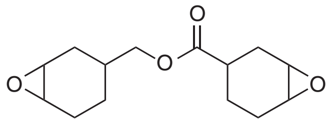


Figure 1.6 Chemical structure of the cycloaliphatic resin (3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate).

the compositions studied, responsible for the increase of their impact strength, was observed.

One of the most important areas of application of epoxidized vegetable oils are compositions with epoxy resins, capable of cross-linking with UV or visible light. Photoinitiated polymerization is a commonly used industrial method of cross-linking of coating materials. Throughout this method, the cured coating is obtained in a short time and above all at the room temperature. Modified natural oils are a very interesting alternative to acrylic monomers, commonly used to obtain photosetting coatings, and starting from the first reports [38] are the subject of the research performed by scientific teams around the world. Compositions consisting of vernonia oil or epoxidized soybean oil and cycloaliphatic epoxy resin were tested [39] (Figure 1.6).

The compositions were cross-linked by photopolymerization using a cationic UV initiator, which was a mixture of triarylsulfonium salts of hexafluoroantimone with a trifunctional primary triol based on ε-caprolactone. Coatings with the addition of epoxidized vegetable oils are characterized by excellent adhesion to the surface, high impact strength, UV stability, corrosion resistance, and long-lasting shine. It was also found that pencil hardness and tensile strength of coating films decrease with increasing oil content. Similarly, the glycidyl castor oil derivative [40], added in an amount of up to 60 wt% to the same cycloaliphatic resin and cross-linked with it using triarylsulfonium salts as cationic initiators (Figure 1.7), leads to a significant improvement of epoxy coating properties: increasing its elasticity and gloss as well as reducing water absorption.

Flexible coatings characterized by high tensile strength and hardness are obtained by adding epoxidized palm oil to cycloaliphatic resin (Figure 1.6) [41]. Additionally, in the described research, the possibility of photopolymerization of prepared compositions with UV light in the presence of various initiators, radical, cationic, and hybrid ones, was tested. Because of the low solubility of triarylsulfonium salts in oil, divinyl ethers of various structures were also added to the composition, which, as it was found in the course of the study, did not affect the mechanical properties of cured coatings. The photocuring process of highly branched resins obtained from modified vernonia oil was also investigated [42]. For the reason that the final properties of cross-linked compositions with

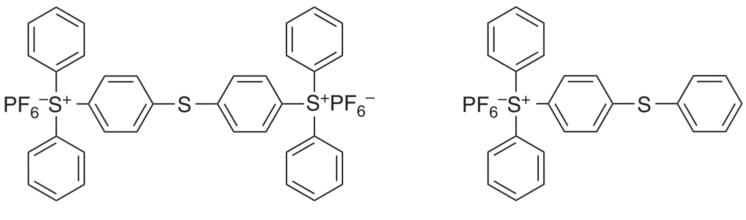


Figure 1.7 Triarylsulfonium salts applied as the cationic photoinitiators.

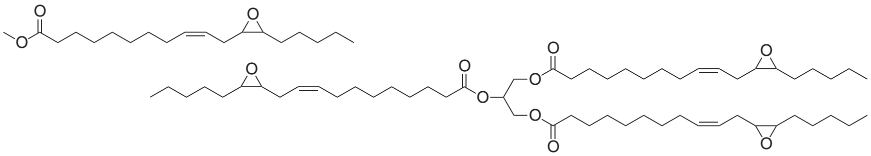


Figure 1.8 Structure of vernolic acid methyl ester and product of its reaction with trimethylol propane.

modified vegetable oils depend not only on the amount of oil but also on their structure, the authors decided to study the photopolymerization of epoxy resin with a strictly defined composition and structure. For this purpose, obtained in the oil transesterification reaction of *Euphorbia lagascae*, methyl vernolate was reacted with trimethylol propane to give the compounds depicted in Figure 1.8.

The obtained derivatives, including the hyperbranched polyether, were used to prepare compositions with different contents of individual components, with methyl vernolate acting as a reactive diluent. The compositions were polymerized with a cationic photoinitiator (octyloxydiphenyliodine hexafluoroantimonate). The application of methyl vernolate reduces the viscosity of the polyether as well as significantly decreases the glass transition temperature. An interesting example of the synthesis of epoxy resin based on vegetable oil, hardened later by the photopolymerization, is the attachment of bicyclo[2.2.1]heptane to linseed oil [43]. The derivative, which is shown in Figure 1.9, was obtained by the Diels–Alder reaction of cyclopentadiene with linseed oil, carried out at the temperature of 240 °C and a pressure of 1.4 MPa.

Compositions consisting of a epoxidized derivative, the addition of various divinyl ethers of epoxidized linseed oil, and cycloaliphatic epoxy resin (Figure 1.6) have been cured using the already mentioned triarylsulfonium salts. Divinyl monomers fulfilled the role of reactive diluents and compatibilizers primarily of oil and photoinitiator. It is also known that the presence of this type of monomers accelerates photocuring of cycloaliphatic epoxy resins. It has been observed that the cross-linking of the cycloaliphatic linseed oil derivative proceeds at a lower rate than the cycloaliphatic epoxy resin, but with a higher rate than epoxidized oil. The addition of divinyl monomers

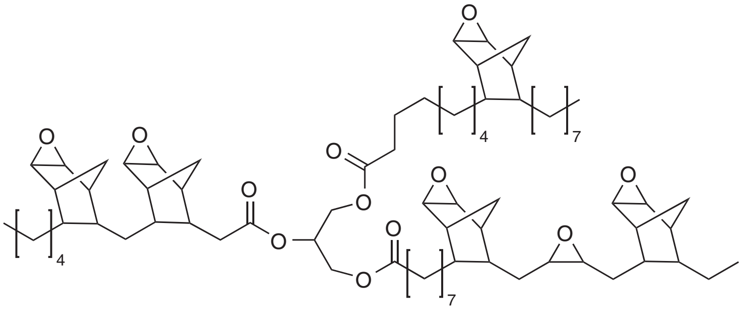


Figure 1.9 Structure of norbornyl epoxidized linseed oil.

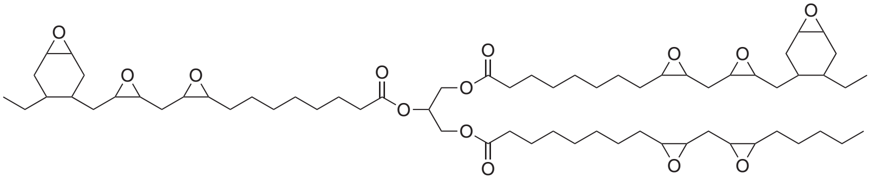


Figure 1.10 Structure of epoxidized cyclohexene-derivatized linseed oil.

accelerates the speed of curing and increases the elasticity of the cured materials. A similar relationship was also observed during kinetic studies of the cationic photopolymerization reaction of a cycloaliphatic linseed oil derivative [44]. It was found that the photo-cross-linking rate is controlled by the diffusion of active macromolecules, which depends on the viscosity of the environment. The different reactivity of the cycloaliphatic and epoxidized oil derivative in the main chains results from the differences in the diffusion of the molecules of both compounds and depends on the presence of divinyl monomers in the reaction environment. The improvement of the final properties of the described compositions was obtained by adding up to 20 wt% of tetraethyl orthosilane (TEOS) [45]. The organic–inorganic hybrid materials obtained in this way, containing the optimum amount of TEOS oligomers, amounting to about 10 wt%, were characterized by the highest value of the elastic modulus, the highest glass transition temperature, and the highest cross-linking density. Although the incorporation of TEOS oligomers in the structure of a cured cycloaliphatic linseed oil derivative simultaneously reduces the relative elongation at break and fracture toughness, it should be remembered that the biggest disadvantages of modified vegetable oils as materials susceptible to photocuring are low glass transition temperature and low speed of cross-linking. Another example of a cycloaliphatic linseed oil derivative, also intended for photocuring, is the product of a Diels–Alder reaction of linseed oil with 1,3-butadiene [46] (Figure 1.10).

Compositions based on modified vegetable oils, hardened by photopolymerization, are mainly intended for coating materials. However, it has been shown that it is also possible to use epoxidized soybean and linseed oils together with cycloaliphatic epoxy resin as binders for glass fiber-reinforced composites and cross-linked with visible or UV light [47].

1.3 Substitutes for Bisphenol A Replacement

1.3.1 Lignin-Based Phenols

Lignin (Figure 1.11) is the relatively large-volume renewable aromatic feedstock. Next to heteropolysaccharides, it is one of the most abundant biopolymer on Earth, which is found in most global plants [48, 49]. It is deposited in the cell walls and the middle lamella.

Lignin, whose concentration systematically decreases from the outer layer to the inner layer of the cell wall, is generally responsible for reinforcing the plant structure. It is described as a water sealant in the stems, playing an important

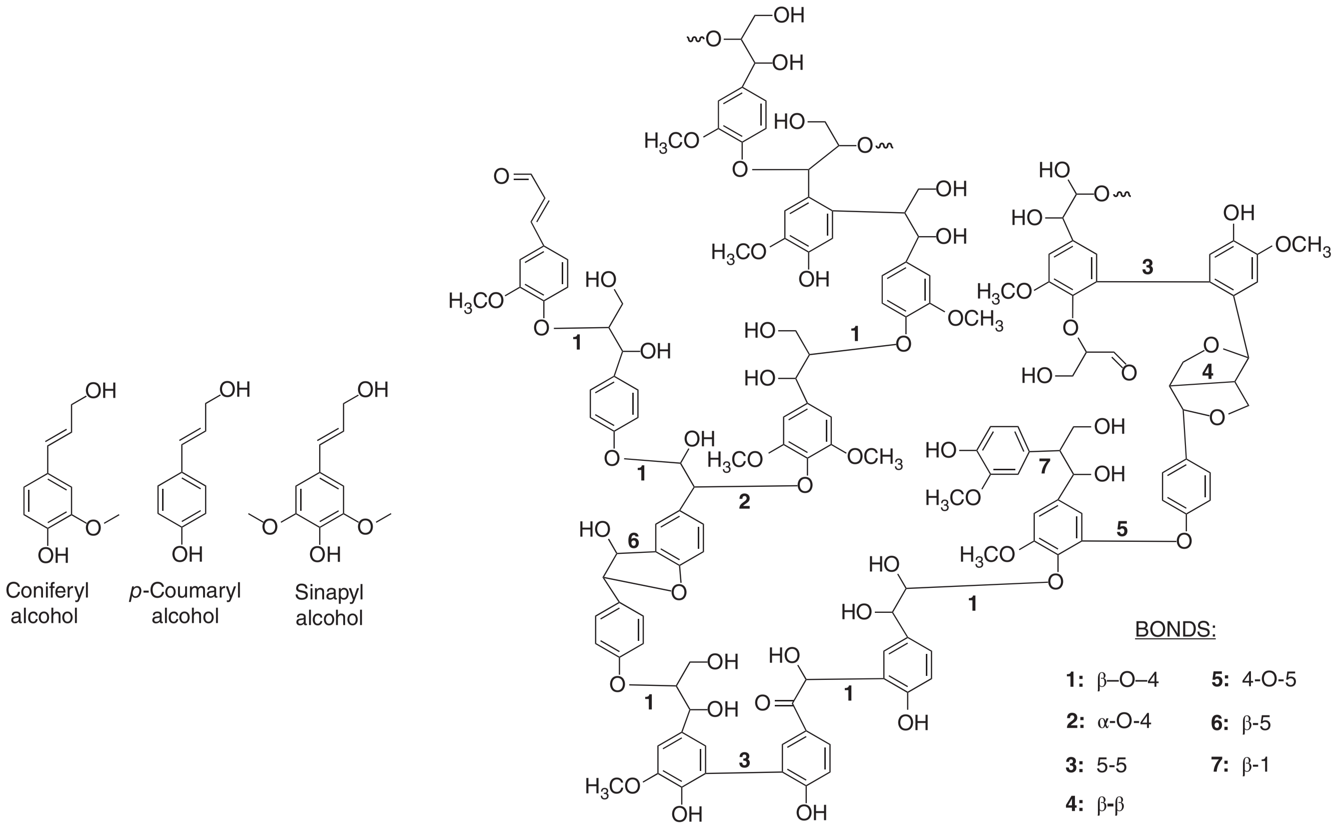


Figure 1.11 Simplified structure of softwood lignin (including three monolignols, the building blocks of lignin) [48, 49].

role in controlling water transport throughout the cell wall. Additionally, lignin of outer layers acts as a binding agent, holding the adjoining cells together, whereas the lignin within the cell walls gives rigidity by the chemical bonding with hemicellulose and cellulose microfibrils [50]. Moreover, it protects plants against decay and biological attacks [51].

Lignin is a complex and amorphous, three-dimensional network of hydroxylated phenylpropane units. Its contents vary with different types of plants, and overall, it is about 15–40% of the dry weight of lignocellulosic biomass [52]. Lignin is cross-linked with cellulose and hemicellulose through covalent and hydrogen bonds [53]. Generally, because of the complex structure and variety of possible degrees of polymerization, lignin is called by the term "lignins," which refers to the complex and diverse chemical composition and structure [54]. Mentioned properties, along with amorphous and hydrophobic nature, have an influence on difficult process of the isolation of lignin in unaltered form [55]. That is why, ball-milled wood lignin (MWL), isolated from finely powdered wood via the application of mild, neutral solvents, is considered to be the closest to *in vivo* lignin. In general, lignins contain a variety of alkyl- or aryl-ether interunit linkages (~60–70%), carbon–carbon (~25–35%), and small amounts of ester bonds, which include β-O-4, β-5, β-β, β-1, β-5, β-6, α-β, α-O-4, α-O-γ, γ-O-γ, 1-O-4, 4-O-5, 1-5, 5-5, and 6-5 (Figure 1.11) [56, 57]. Respectively, β-O-4-aryl ether (β-O-4), β-O-4-aryl ether (β-O-4), 4-O-5-diaryl ether (4-O-5), β-5-phenylcoumaran (β-5), 5-5-biphenyl (5-5), β-1-(1,2-diarylpropane) (β-1), and β-β (resinol) are major linkages, which are present within lignin macromolecules.

The lignin content is usually higher in softwoods (27–33%) than in hardwoods (18–25%), and herbaceous plants such as grasses (17–24%) have the lowest lignin contents [51]. Moreover, lignin originated from softwood and hardwood has different contents of methoxyl groups. Softwood lignin is composed of guaiacyl units, resulted from a polymerization of coniferyl alcohol (one methoxyl group per phenylpropane unit), whereas hardwood lignin is a copolymer of coniferyl and sinapyl alcohols (two methoxyl groups per phenylpropane unit). Additionally, hardwood lignin, on the one hand, contains fewer free phenolic hydroxyl groups but, on the other hand, contains more free benzyl alcohol groups than softwood lignin (Table 1.2).

Based on the literature [58], there is also a third type of lignin, which is formed by the polymerization of *p*-coumaryl alcohol. However, the resulting *p*-hydroxyphenyl lignin, is usually found in the form of a copolymer with guaiacyl lignin only in certain trees and tissues.

Even though lignin is one of the most abundant natural polymers, its industrial applications are rather limited. That is why, recently, in the era of greater ecological awareness, as well as unstable and diminishing petrochemical resources, the intensive research is being performed on application of lignin and its valuable compounds. However, the strong chemical bonding of lignin with hemicellulose and cellulose microfibrils makes it hard to isolate for effective utilization. Hence, great effort is being put on the development of pretreatment methods for more effective separation of lignin. Generally, the isolation of lignin is performed by its extraction using different methods, such as Kraft, soda, lignosulfate,

Table 1.2 Proportions of interunit linkages in softwood and hardwood [50].

	Lignocellulosic material	
Structure (%)	**Softwood**	**Hardwood**
Phenylpropane unit		
– Coumaryl	—	—
– Coniferyl	90–95	50
– Sinapyl	5–10	50
C_9-O-C_9		
– β-O-4	46	60
– α-O-4	6–8	6–8
– 4-O-5	3.5–4	6.5
C_9-C_9		
– β-5	9–12	6
– β-1	7	7
– β-β	2	3
– 5-5	9.5–11	4.5

organosolv [59–61], hydrolysis, enzymatic, ionic liquids [62], and ultrafiltration by membrane technology. Because all the mentioned isolation methods require specific conditions such as pH, temperature, pressure, reagents, time, and variety of different solvents, the isolated lignin is characterized by diverse structural and chemical properties [63]. Utilization of lignin might be performed: (i) without its chemical modification (via the incorporation of lignin into matrix to give new or improved properties) and (ii) with the chemical modification to prepare a large number of smaller chemicals, which might be used to obtain other chemical compounds including polymers. The chemical modification of lignin (Figure 1.12) is performed by (i) fragmentation or lignin depolymerization to use lignin as a carbon source or to split the structure of lignin into aromatic macromers; (ii) creation of new chemical active sites, and (iii) chemical modification of hydroxyl groups.

Nearly 90% of epoxy polymers are obtained from bisphenol A (BPA). However, there is a growing demand to develop renewable aromatic compounds to replace the petroleum-based BPA. Conducted studies are concentrated on maintenance in bio-based materials the desirable thermomechanical properties, provided by aromatic rings of BPA-based epoxy resins, which are linked to the rigidity provided by aromatic rings of BPA. That is why, efforts in the synthesis of novel epoxy resins are mainly directed toward renewable phenolic compounds derived from biomass feedstocks. Lignin is one of the most promising natural resource for replacement of bisphenol A because of the presence of aromatic structure with hydroxyl, carboxylic acid, and phenolic functional groups, which are able

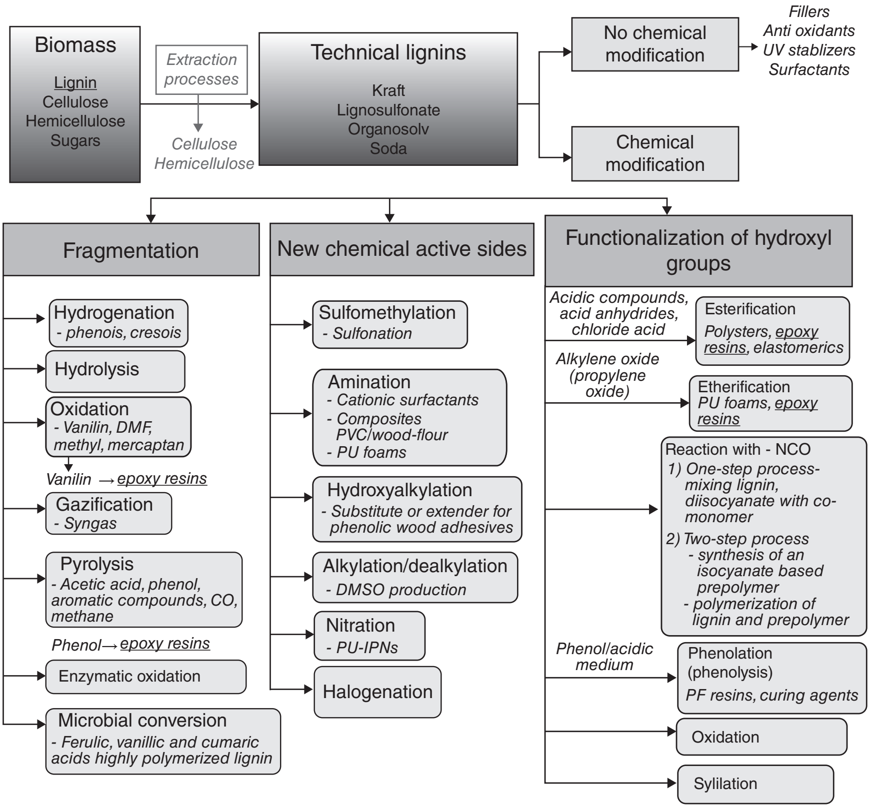


Figure 1.12 Summary of the main strategies for lignin conversion [49, 55].

to react with epichlorohydrin to form bio-based epoxy resins. The phenolic and alcohol hydroxyls, which are present within the lignin macromolecule, have found application in numerous research on incorporating that biopolymer into thermosetting resins, either as a component during the synthesis of epoxy monomers or as a reactive additive [64]. In general, the process of preparation of lignin-based epoxy resins might be conducted by (i) direct blending of lignin with epoxy resin [65], (ii) modifying lignin derivatives by the glycidylation [66], or (iii) modifying lignin derivatives to improve their reactivity, followed by the glycidylation [67]. Recently, one of the most common approaches to obtain lignin-derived polyols is the lignin depolymerization to lower molecular weight compounds, such as vanillin, vanillyl alcohol derivatives [68], phenol [69], isoeugenol [70], syringaresinol, and compounds based on propyl guaiacol and its demethylated product.

Bio-based epoxy resins are, for instance, synthesized from derivatives obtained on the course of lignin hydrogenolysis [71]. Lignin from pine wood is depolymerized by mild hydrogenolysis to give an oil product, containing aromatic polyols: dihydroconiferyl alcohol (DCA, 4-(3-hydroxypropyl)-2-methoxyphenol) and 4-propyl guaiacol (PG, 4-propyl-2-methoxyphenol), along with their dimers and

Table 1.3 Thermal analysis data for epoxy resin blends containing DGEBA and cured with DETA [68].

Resin	T_g [a] (°C)	$T_{5\%}$ [b] (°C)	T_s [c] (°C)
DGEBA	117	328	169
LHEP/DGEBA 1 : 1	80	289	161
LHEP/DGEBA 2 : 1	70	270	156
LHEP/DGEBA 3 : 1	68	258	151
LHEP	53	236	144

a) T_g – the glass transition temperature.
b) $T_{5\%}$ – the initial decomposition temperature.
c) T_s – the statistic heat-resistant index temperature.

oligomers. Then, the obtained oil product is dissolved in refluxing epichlorohydrin in the presence of solution of NaOH to give epoxy prepolymer (LHEP) (Figure 1.13), which is then blended with bisphenol A diglycidyl ether (DGEBA) in mass ratios of LHEP : DGEBA up to 3 : 1. Epoxy composition might be cross-linked with diethylenetriamine (DETA).

Cured epoxy material LHEP/DGEBA is less thermally stable than the DGEBA resin (Table 1.3) because of the presence of methoxy groups on the aromatic ring.

The initial decomposition temperature ($T_{5\%}$) and the statistic heat-resistant index temperature (T_s) are the lowest for samples containing the highest proportion of LHEP. On the other hand, the presence of methoxy groups in the lignin hydrogenolysis products is likely to contribute to the superior mechanical properties of the cured LHEP/BADGE blends. Values of flexural modulus and strength of bio-based materials are 52% and 28%, respectively, greater than DGEBA alone. Additionally, it is worth to mention here the research on the influence of the presence of lignin on the thermal performance and thermal decomposition kinetics of lignin-based epoxy resins [72]. The presence of lignin-based epoxy resin (depolymerized Kraft lignin, DKL-epoxy resin, and depolymerized organosolv lignin, DOL-epoxy resin, respectively) in epoxy composites, prepared by mixing the DGEBA and a desired amount (25, 50, and 75 wt%) of DKL-epoxy resin and DOL-epoxy resin at 80 °C, then cured with 4,4′-diaminodiphenylmethane (DDM), results in a significant effect on the activation energy of the decomposition process, in particular, at the early and the final stage of decomposition (Table 1.4).

The increase in the percentage value of lignin-based epoxy resins in the composites reduces the initial activation energy of the system. Additionally, the obtained bio-based materials exhibit higher limiting oxygen index (LOI) than that of the conventional BPA-based epoxy resin, which might indicate that the lignin-based epoxy composites are more effective fire retardants than the conventional BPA-based epoxy resin.

An interesting example of a novel approach to finding new epoxy application for bio-based derivatives from lignin is a conversion of lignin to epoxy compounds throughout the reaction of epichlorohydrin with partially depolymerized

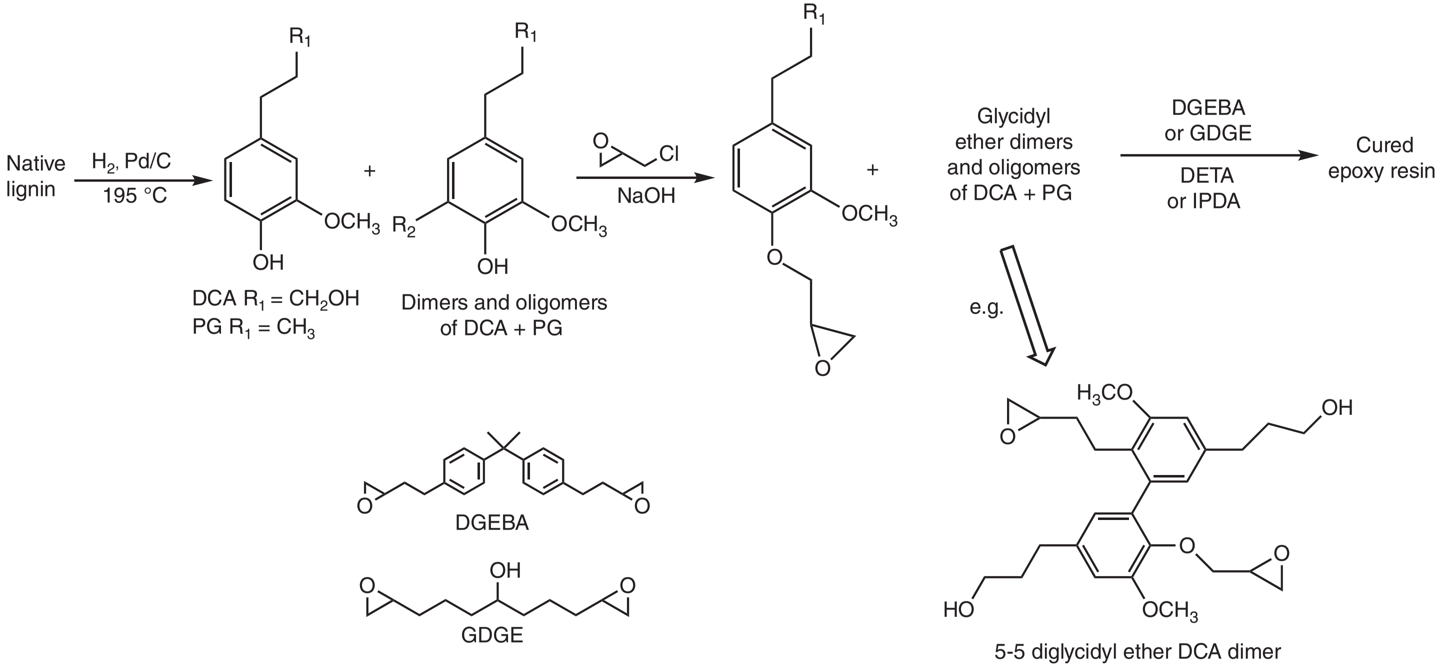


Figure 1.13 Cured epoxy resins from lignin hydrogenolysis products.

Table 1.4 Thermal decomposition of BPA-based epoxy resin and the DGEBA/lignin-based epoxy resin [72].

Sample	IDT (°C)	T_{max} (°C)		Char$_{800}$ (%)	LOI
		Shoulder peak	Main peak		
DGEBA-DDM	370	—	405	12.5	22.5
25% DKL-DDM	359	—	397	18	24.7
50% DKL-DDM	330	—	396	25	27.5
75% DKL-DDM	300	335	407	32	30.3
100% DKL-DDM	290	325	416	38	32.7
25% DOL-DDM	383	—	404	17	24.3
50% DOL-DDM	352	—	399	21	25.9
75% DOL-DDM	338	—	398	24	26.7
100% DOL-DDM	335	—	397	29	29.1

lignin (PDL) in the presence of benzyltriethylammonium chloride and dimethyl sulfoxide (Figure 1.14) [67].

The lignin-based epoxy material is characterized by comparable thermal and mechanical properties to those of BPA-based epoxy resin (DER332) cured with the same bio-based curing agent (the Diels–Alder adduct of methyl esters of eleostearic acid, a major tung oil fatty acid, and maleic anhydride [MMY]). The obtained bio-based epoxy product might be applied as a modifier for asphalt applications in the same manner as petroleum-based (and mostly BPA-based) epoxy resins, which are currently used for asphalt modification to improve its temperature performance. The PDL epoxy asphalt, in the same way as DER332-asphalt, exhibits significant improvement on the viscoelastic properties, especially at elevated temperatures.

The research on utilization of lignin derivatives toward the synthesis of the epoxy system is ongoing for several years; thus, there are numerous methods described in the literature. Among them, it is worth to mention the synthesis of epoxies by (i) direct epoxidation of the phenolic hydroxyl group in the technical lignin with epichlorohydrin and (ii) obtaining bisguaiacyl structure via the reaction using ketone compound and then the epoxidation (Figure 1.15a) [66].

The other route of lignin utilization toward the synthesis of epoxy system is the cleavage of lignin intermolecular bond and creating the phenolic hydroxyl group in the molecule (Figure 1.15c). The process is usually done by treating the Kraft lignin with acid (hydrochloric or sulfuric acid) and phenol derivatives. The obtained phenolic hydroxyl group is epoxidized with epichlorohydrin, resulting in the lignin-based epoxy resin, which in the next step is cross-linked using DETA or phthalic anhydride. The phenol derivative within the lignin structure might also be obtained on the course of the lignin phenolization with bisphenol A in the presence of hydrochloric acid and BF_3-ethyl etherate as catalysts (Figure 1.15b) [73]. The obtained product is soluble in organic solvent such as acetone because of the contribution of bisphenol A.

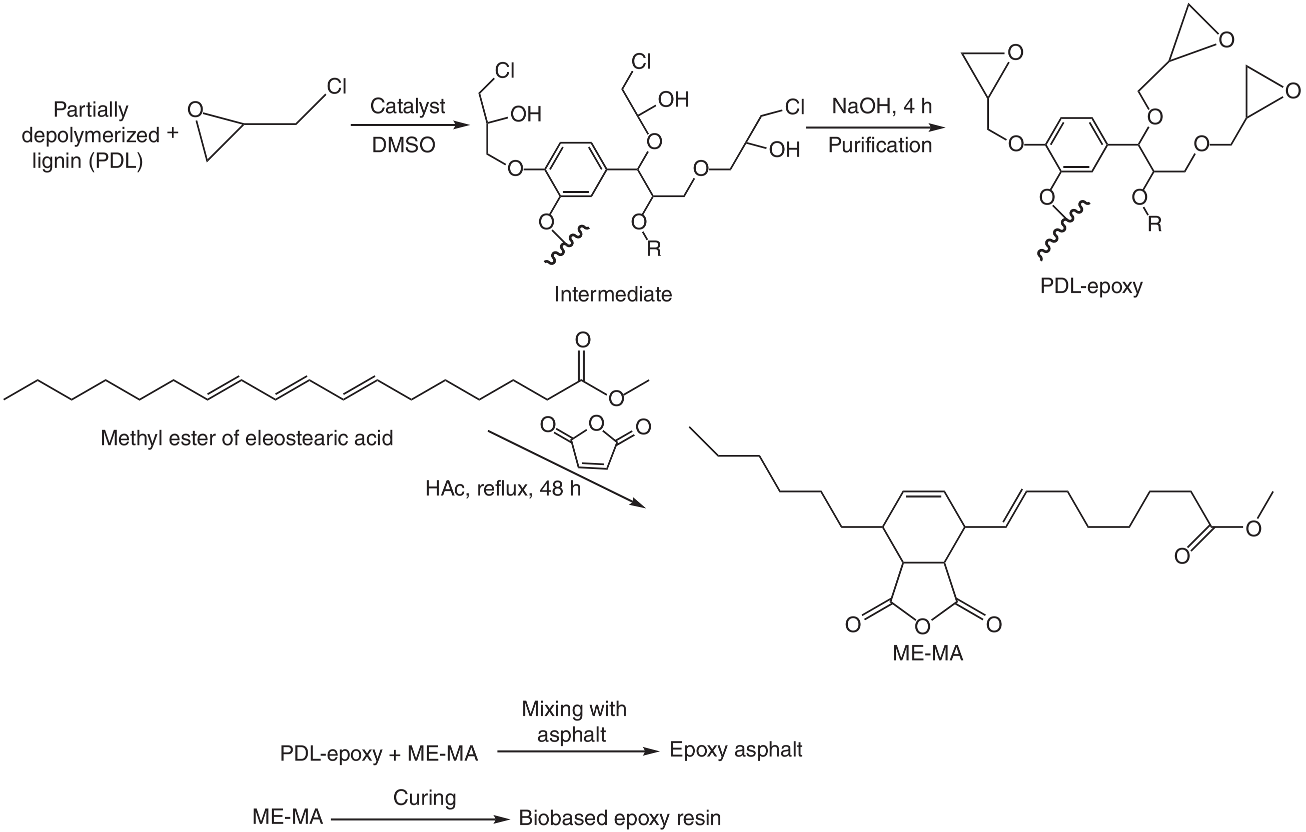


Figure 1.14 Synthesis of lignin-based epoxy and epoxy asphalt.

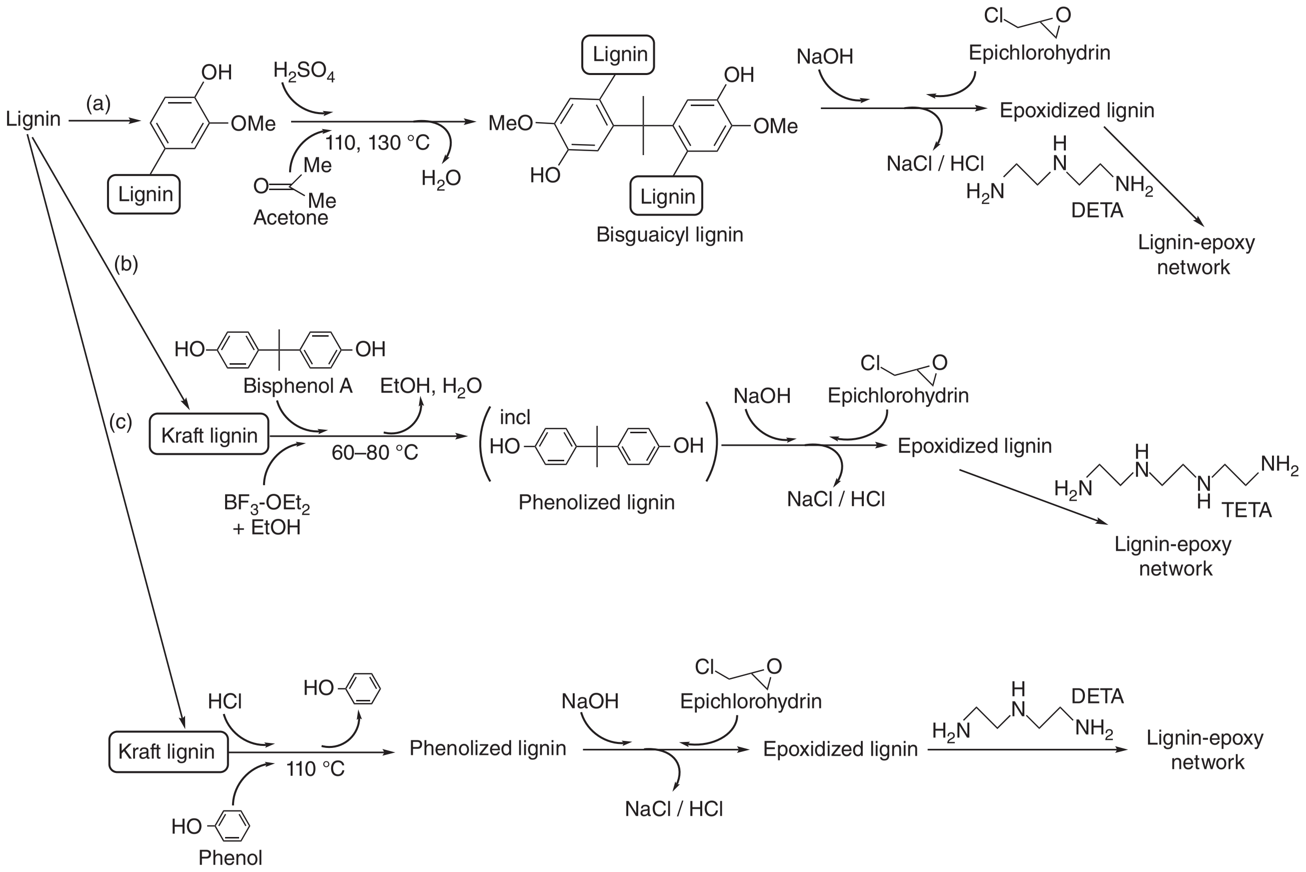


Figure 1.15 Schematic routes of lignin modification and crosslinking: (a) epoxidation with bisguaiacyl structure stage, (b) lignin' phenolization with bisphenol A and (c) direct epoxidation of the phenolic hydroxyl group in the technical lignin with epichlorohydrin.

It is worth noting that a substantial amount of lignin decomposing aromatics is characterized by the structure of phenol substituted by inert methoxy and alkyl groups (structures such as guaiacol or creosol), making polycondensation or radical polymerization especially difficult. Thus, there are numerous studies on (i) introducing the reactive groups, which are promoting further polymerization reactions [74], (ii) utilization of the reactive *ortho-* and *para-*sites of phenol for hydroxymethylation or obtaining novolac or resol-type resin using formaldehyde chemistry [75] otherwise, (iii) connecting lignin-derived compounds to make oligomers with additional functional groups [76]. Bimetallic Zn/Pd/C catalytic method for converting lignin via the selective hydrodeoxygenation ($T = 150\,°\mathrm{C}$ and 20 bar H_2, using methanol as a solvent) directly into two methoxyphenol products has been reported [77]. The compound characterized by the increased content of hydroxyl groups might be obtained using the above method, via the reaction of *o*-demethylation of 2-methoxy-4-propylphenol and aqueous HBr. In the next step, propylcatechol is glycidylated to epoxy monomer (Figure 1.16).

Other techniques described in the literature involve the ozone oxidation of Kraft lignin toward splitting its aromatic rings and generation of the muconic acid derivatives. The ozonized lignin (Figure 1.17a) might then be dissolved in an alkali water solution and cross-linked with the water-soluble epoxy resin (glycerol polyglycidylether).

Another interesting synthesis described in the literature begins from the dissolution of alcoholysis lignin or lignin sulfuric acid in ethylene glycol and/or glycerin (Figure 1.17b) [78]. Next, the hydroxyl group in the lignin molecule is reacted with succinic acid to convert the lignin into multiple carboxylic acid derivatives. In the last step, the resulting products react with epoxy compound (ethylene glycol diglycidyl ether [EGDGE]) in the presence of dimethylbenzyl amine as a catalyst to provide the cross-linked epoxidized lignin resin. In the obtained curried epoxy material, lignin acts as a hard segment (increasing value of T_g with increasing lignin derivatives). Additionally, a slight decrease of T_d with increasing content of biocomponent in epoxy resin suggests that the thermal stability of obtained epoxy system is not affected by the presence of lignin derivatives.

Based on numerous studies, one can conclude that lignin is a very promising natural resource for replacement of bisphenol A in the synthesis of epoxy resins, as it has aromatic structure with hydroxyl, carboxylic acid, and phenolic functional groups, which can react with epichlorohydrin to form bio-based epoxy resins. One of the biggest problems for commercial application of lignin's derivatives, because of its complex and multifunctional nature, is isolation and the synthesis of monomers.

1.3.2 Vanilin

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is an organic compound consisting of a benzene ring substituted with three functional groups: aldehyde –CHO, hydroxyl –OH, and methoxy $–O–CH_3$ (Figure 1.18a).

It is a naturally occurring compound (in the form of its β-ᴅ-glucoside, Figure 1.18b) that can be directly obtained in the extraction process from the bean or seed pods of *Vanilla planifolia*, the tropical orchid presently cultivated

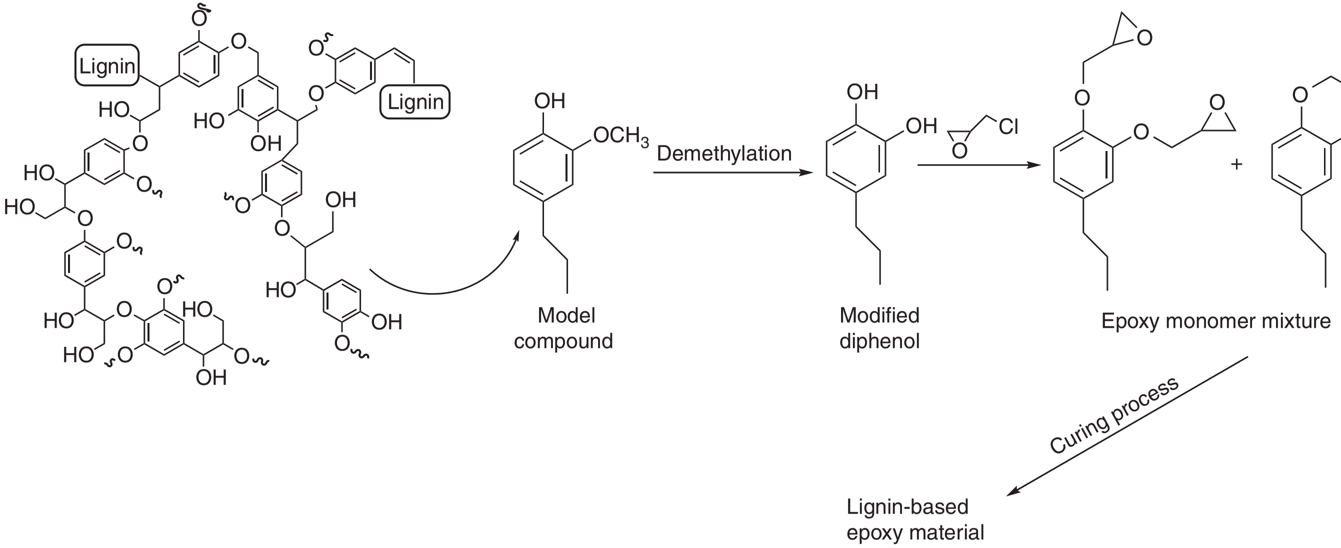


Figure 1.16 Route of the synthesis epoxy monomers from selectively hydrodeoxygenated lignin.

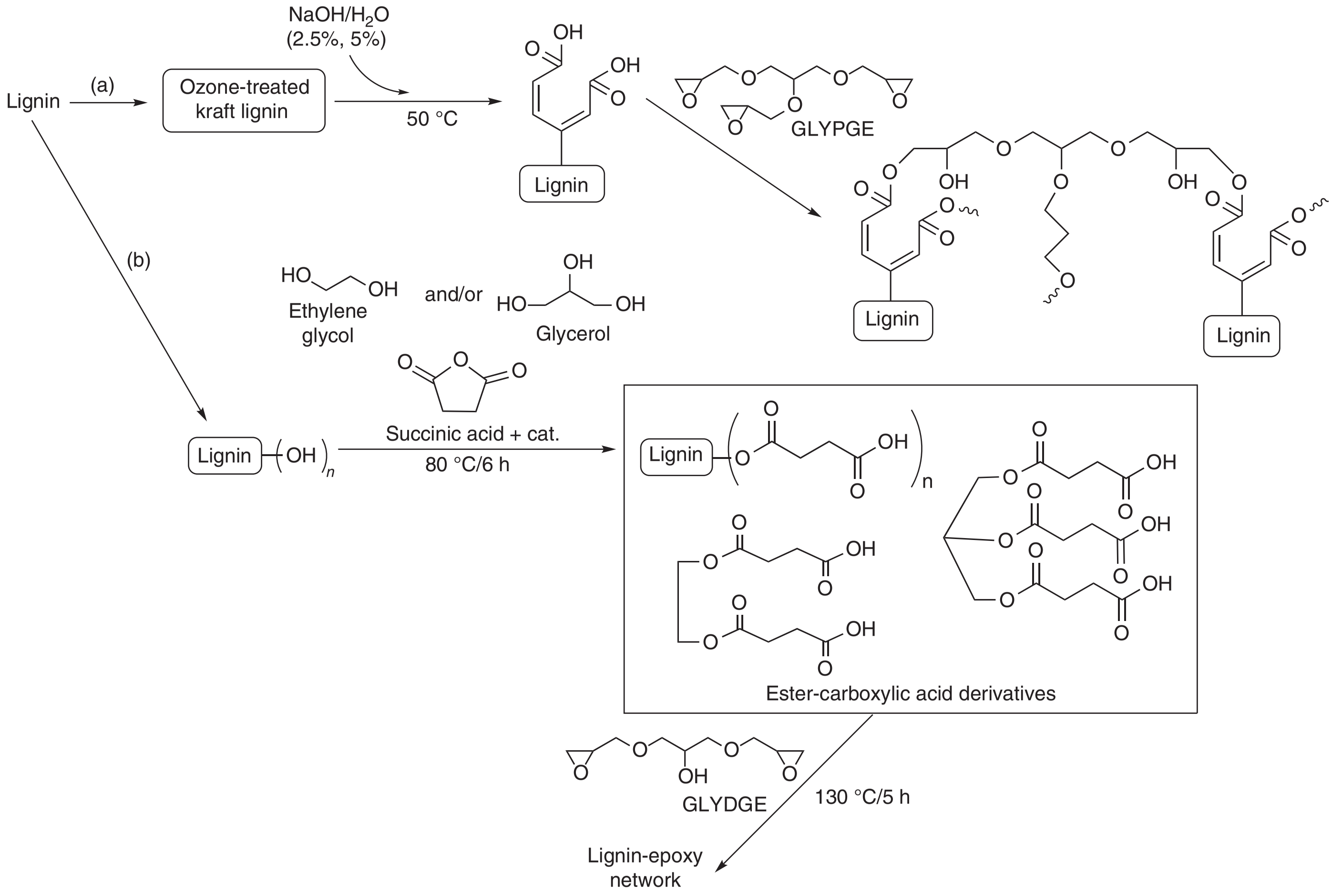


Figure 1.17 Lignin modification and cross-linking: (a) ozone oxidation of Kraft lignin and (b) synthesis of multiple carboxylic acid derivatives.

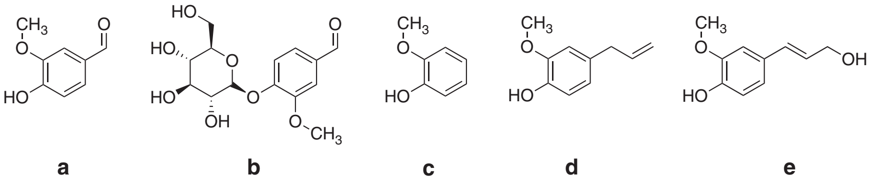


Figure 1.18 Chemical structures of (**a**) vanillin and its naturally occurring precursors: (**b**) vanillin glucoside, (**c**) guaiacol, (**d**) eugenol, and (**e**) coniferyl alcohol.

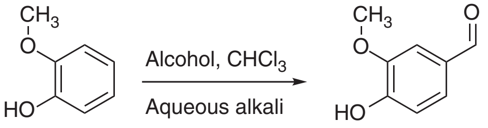


Figure 1.19 Synthesis of vanillin from guaiacol.

in a number of tropical countries. Although this method has been known for centuries and it is still used, actually less than 1% of vanilla produced in the world is obtained in such a way [79]. Almost all vanillin is now synthesized much more cheaply through chemical processes. Synthetic vanillin is commercially available and is commonly used in both food and nonfood applications, in fragrances, as a flavoring in pharmaceutical preparations, as an intermediate in the chemical and pharmaceutical industries for the production of herbicides, antifoaming agents or drugs, and in household products, such as air fresheners and floor polishes. Synthetic or semisynthetic vanillin can be derived from two compounds: guaiacol and eugenol, both available from petrochemical sources or of natural origin.

The first one, guaiacol (2-methoxyphenol) (Figure 1.18c), is a naturally occurring organic compound present in an aromatic oil from flowering plants *Guaiacum*. Guaiacol can also be gained from creosotes formed by distillation of various tars and pyrolysis of plant-derived material, such as wood. Semisynthetic vanillin can be obtained from guaiacol through the Reimer–Tiemann reaction of phenols formylation (Figure 1.19) [80].

The reaction is carried out using chloroform deprotonated by a strong base (hydroxide typically) to form the chloroform carbanion and finally the dichlorocarbene, which is the principal reactive specie in nucleophilic substitution also occurred in deprotonated phenol. Another method of vanillin synthesis from guaiacol is its reaction with glyoxylic acid (Figure 1.20a), leading to the formation of 2-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-acetic acid (Figure 1.20b) [81]. The obtained vanillylmandelic acid is converted via 2-(4-hydroxy-3-methoxyphenyl)-2-oxoacetic acid (Figure 1.20c) to vanillin by the oxidative decarboxylation [82].

Eugenol (2-methoxy-4-(prop-2-en-1-yl)phenol) (Figure 1.18d) present in an essential oil extracted from the clove plant *Syzygium aromaticum* is the next important natural raw material for the vanillin synthesis (Figure 1.21).

The synthesis consists of two steps: the basic isomerization of the double bond in eugenol leading to the formation of isoeugenol and oxidation of the rearranged

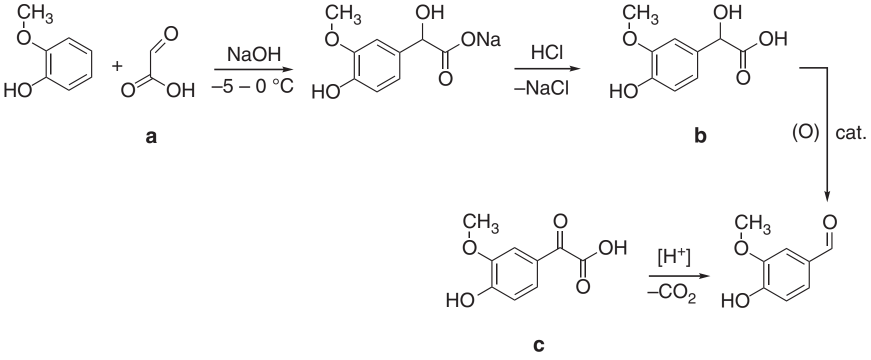


Figure 1.20 Synthesis of vanillin from guaiacol using glyoxylic acid.

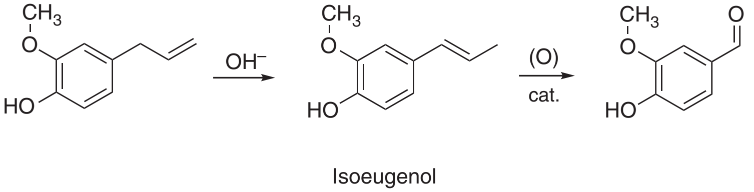


Figure 1.21 Synthesis of vanillin from eugenol.

double bond to vanillin [83, 84]. The process can be carried out with or without isolation of the intermediate product which is isoeugenol [85].

Lignin from softwood is still one of the most important sources of raw materials for the synthesis of vanillin. Three-dimensional network structures of lignin are composed of three types of monolignols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Coniferyl alcohol (Figure 1.18e) is the main intermediate in the pathways to vanillin from a softwood (coniferous) lignin, as well as the precursor for eugenol in its biosynthesis. Vanillin can be produced from the lignin-containing waste manufactured by the sulfite pulping process for preparing wood pulp for the paper industry [86]. This first developed method of vanillin synthesis from lignin lost its relevance primarily for environmental reasons (the need to safely get rid of alkaline-based liquid waste). However, thanks to the results of work on the process optimization [87], it was possible to achieve an increase in the yield of vanillin and a reduction in waste stream volume. Therefore, the volume of vanillin production from lignin is still estimated at around 15% of the total world vanillin production.

There are also known for years [88] and still developed biotechnological processes of vanillin synthesis [89]. They are promising for the industrial-scale production of vanillin due to the use of natural raw materials, renewable and readily available in large quantities, such as rice bran [90] or corn sugar [91]. However, actually bio-synthesized vanillin is still very expensive [92] and its high cost of production are justified only for specific applications in the food, cosmetics, and pharmaceutical industries. Nowadays, the biotechnological

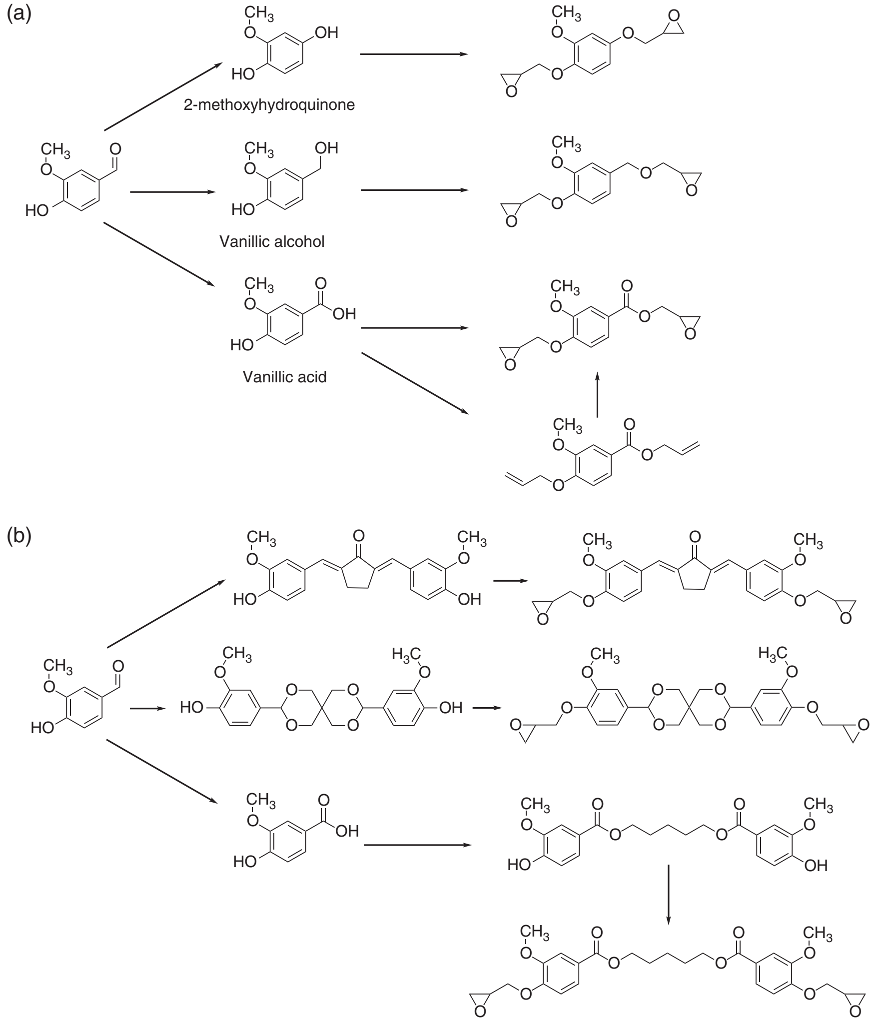


Figure 1.22 Schematic illustration of possible synthesis pathways (a) and (b) for vanillin-based epoxy resins.

production is not suitable and profitable source of vanillin for the synthesis of polymeric materials.

Due to its chemical structure as a phenolic compound, vanillin is the promising raw material that could replace bisphenol A (or other commonly used bisphenols) providing epoxy resins with adequate mechanical strength and thermal stability. However, as the trifunctional compound, but also only a monoalcohol, vanillin must be modified in order to serve as a substitute for bisphenols in the synthesis of epoxy resins. Figure 1.22 shows schematically the possible pathways of vanillin modification described in the literature that lead to obtaining epoxy resins.

Generally, two strategies for the synthesis of vanillin-based epoxy resins are mainly being investigated. The first one (Figure 1.22a) assumes converting

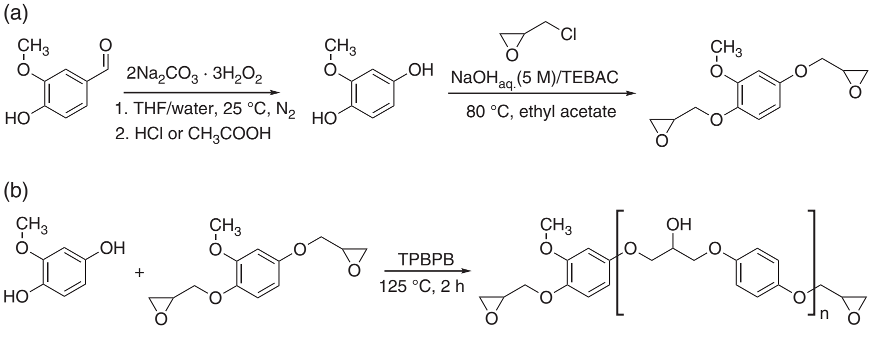


Figure 1.23 Synthesis of 2-methoxyhydroquinone and its epoxy derivatives - strategies (a) and (b).

vanillin into derivatives also containing, in addition to the phenol group already present in the vanillin molecule, a second functional group through which the epoxy functionality could be introduced. The second strategy (Figure 1.22b) involves coupling of two vanillin (or its derivative) molecules using another chemical compound, resulting in a product containing at least two phenolic or other groups through which the epoxy group can also be introduced. In both strategies, commonly used methods for introducing epoxy functionality have been applied: the oxidation of double bonds and the reaction with epichlorohydrin.

According to the first strategy, the Dakin oxidation can be applied to convert aldehyde group in vanillin to hydroxyl group [93] (Figure 1.23).

Synthesized 2-methoxyhydroquinone can be reacted with the large excess (10-fold) of epichlorohydrin under the typical phase-transfer catalysis conditions in the presence of triethylbenzylammonium chloride (TEBAC). The resulting product mainly contains diglycidyl ether of 2-methoxyhydroquinone (Figure 1.23a), which can be used together with 2-methoxyhydroquinone to obtain an epoxy resin (with an epoxy value of 0.060–0.340 mol/100 g) via the fusion process [94] in the presence of triphenylbutylphosphonium bromide (TPBPB) (Figure 1.23b). Such epoxy resin with an epoxy value of 0.404 mol/100 g [95] could be successfully cross-linked with the cycloaliphatic amine curing agent (commercial product Epikure F205), preferably in the presence of calcium nitrate as an accelerator. The vanillin-based epoxy resin cured using 2 wt% of the inorganic accelerator exhibits the tensile strength and the Izod impact strength higher than those for liquid diglycidyl ether of bisphenol A (epoxy resin Epon 828 with an epoxy value of 0.541 mol/100 g) used for comparison. As an aldehyde, vanillin can be easily oxidated to vanillic acid, as well as reduced to vanillic alcohol (Figure 1.22a). Under analogous conditions as in the case of 2-methoxyhydroquinone, the diglycidyl monomers (Figure 1.22a) can be obtained from both vanillic acid and alcohol [96]. After cross-linking with isophorone diamine bio-based epoxy resins derived from them are characterized by the high glass transition temperature (132 and 152 °C, respectively) and the storage modulus comparable with the value determined for diglycidyl ether of bisphenol A. They also exhibit high thermal stability, typical for epoxy resins

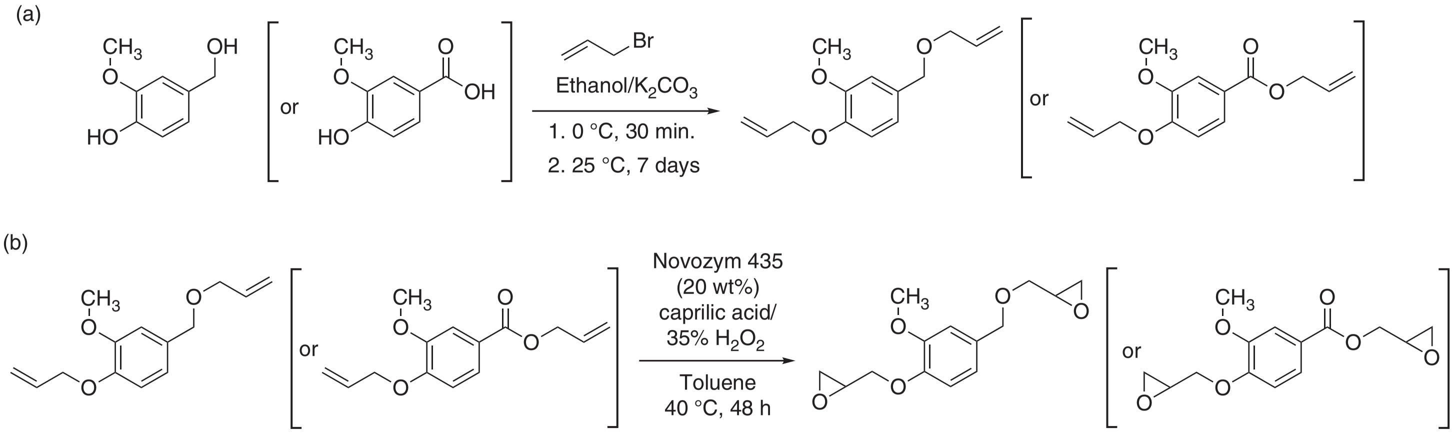


Figure 1.24 The *O*-alkylation of vanillin derivatives (a), followed by the epoxidation of the resulting double bonds (b).

based on bisphenol A. 2-Methoxyhydroquinone as well as vanillic alcohol and acid could be reacted with allyl bromide giving derivatives (Figures 1.22a and 1.24a) with terminal unsaturated bond [97], which can be e.g. enzymatically oxidized to oxirane rings using percaprylic acid as an oxygen carrier and immobilized lipase B from *Candida antarctica* (Novozym 435) as a biocatalyst [98] (Figure 1.24b).

This is another interesting reaction pathway for the synthesis of above-mentioned diglycidyl monomers without using bisphenol A and epichlorohydrin, and under mild conditions. Moreover, the other interesting epoxy compound derived from two coupled vanillic acid molecules (Figure 1.25) could also be prepared throughout this way.

However, obtaining the completely epoxidized products and the formation of various regioisomers still remain challenging.

According to the second strategy, the dimerization of vanillin is possible [99] by the selective enzymatic oxidative coupling (Figure 1.26a). After the reduction of aldehyde groups, a divanillin alcohol is obtained, which can be then reacted with epichlorohydrin (Figure 1.26b) [100].

The vanillin-based epoxy compounds are obtained as a mixture of glycidyl derivatives at different ratios, which can be fractionated by flash chromatography. The content of individual glycidyl derivatives in the product mixture can be controlled primarily by the sodium hydroxide content, as well as the duration of the second step reaction with epichlorohydrin (adding a base at room temperature in order to perform the ring closure of intermediate halohydrin species). For example, with a NaOH/OH ratio equal to 10, the tetraglycidyl compound is mainly obtained with about 90% yield. In contrast, the diglycidyl derivative is mainly created (80% yield) at lower NaOH/OH ratios. Separated vanillin-based epoxy compounds cross-linked with isophorone diamine, characterized with the glass transition temperature in terms of 138–198 °C, exhibit similar Young modulus and thermal stability values to the bisphenol A-based epoxy thermoset, but lower elongation at break.

The other possibility of the vanillin dimerization is the electrochemical synthesis of *meso*-hydrovanilloin (Figure 1.27) [101]. The symmetrical compound divanillin (two molecules of vanillin coupled by aromatic rings) can be easily prepared by the oxidative dimerization of vanillin catalyzed by $FeCl_3$ or heme iron enzymes [102]. However, vanillin can also be reductively dimerized at the aldehyde function using low-valent titanium generated via $TiCl_4$-Mn or by the electrochemical method [103]. The electrochemical coupling is a highly stereoselective reaction giving *meso*-hydrovanilloin. The vanillin electrolytic reduction in alkaline solution at a metallic cathode gives interesting bisphenol compound, which can be used as a direct substitute for bisphenol A [104].

The obtained *meso*-hydrovanilloin-based epoxy resin cured using long-chain aliphatic diamine (1,6-diaminohexane) and cycloaliphatic amine (isophorone diamine) showed the glass transition temperature and Shore hardness (D-type) values comparable with commercial diamine-cured bisphenol A-based epoxy resins.

Two molecules of vanillin can be coupled by the crossed aldol condensation (Figure 1.28) with cyclopentanone [105].

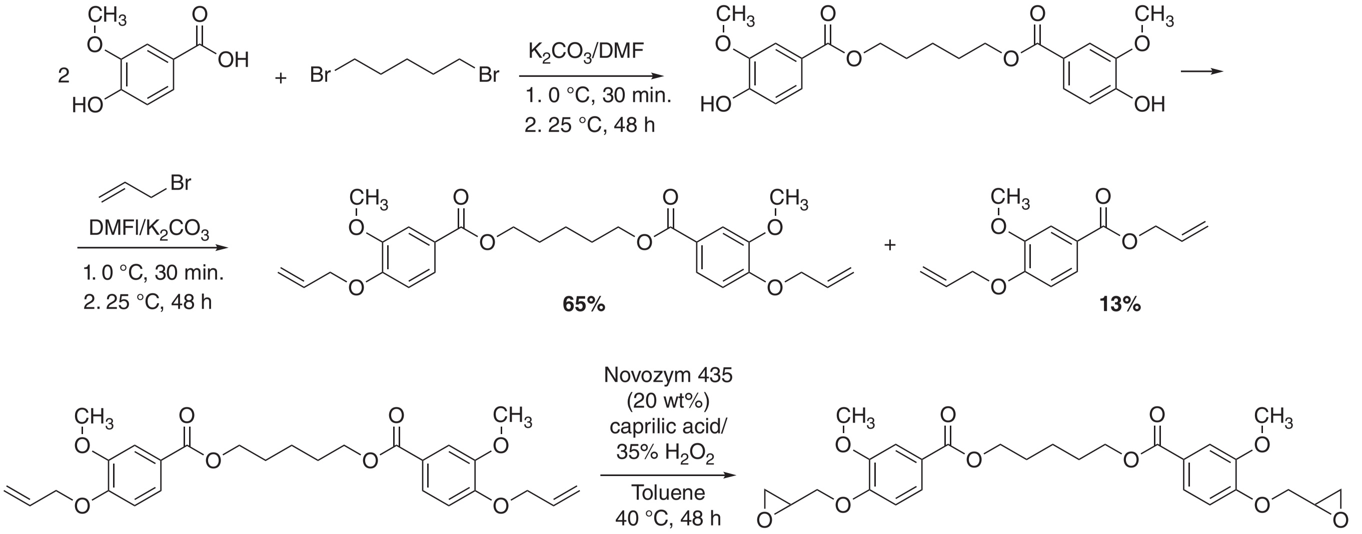


Figure 1.25 Esterification of vanillic acid, followed by the *O*-alkylation and subsequently by the epoxidation of the allylic double bonds.

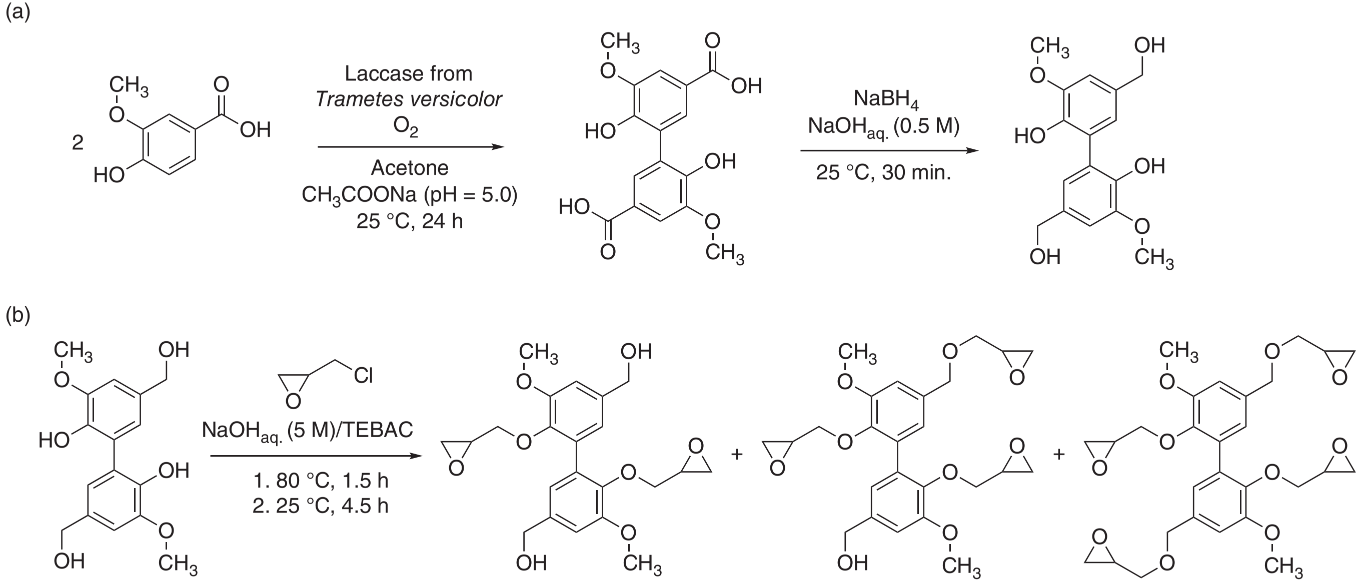


Figure 1.26 Synthesis of glycidyl derivatives (b) based on the product of vanillin dimerization (a).

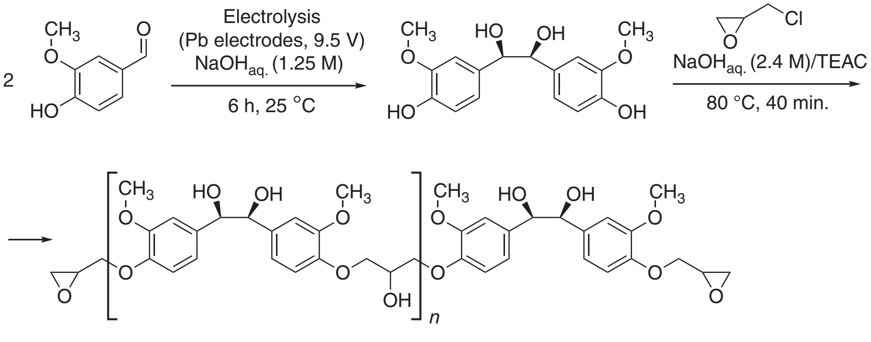


Figure 1.27 Synthesis of hydrovanilloin and the epoxy resin based on this vanillin dimer.

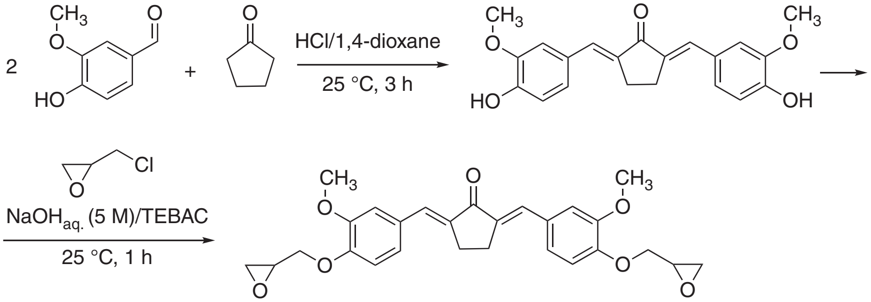


Figure 1.28 Synthesis of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone and its diglycidyl derivative.

The thermal and mechanical properties of the synthesized resin cured with bio-based (quercetin and guaiacol novolac) hardeners and a petroleum-based hardener (phenol novolac) are comparable with those of the bisphenol A-based resins cross-linked with the same hardeners.

A diamine can also be used to couple two vanillin molecules [106]. Vanillin coupled with aromatic diamines and diethyl phosphite, followed by the reaction with epichlorohydrin, yields high-performance biorenewable and environment-friendly flame-retardant epoxy resins (Figure 1.29).

The coupling product with 4,4-diaminodiphenylmethane (DDM) or *p*-phenylenediamine (PDA) is synthesized (Figure 1.29a) through Schiff base condensation, and the generated Schiff base is further reacted with diethyl phosphite by the phosphorus–hydrogen addition reaction to yield phosphorus-containing vanillin-based bisphenols. The resulted bisphenol can be converted into diglycidyl derivative via the above-described reaction with an excess of epichlorohydrin, preferable under PTC conditions. The reactivity of the epoxy resins synthesized in this way is similar to the bisphenol A-based epoxy resin. After curing with a stoichiometric amount of 4,4-diaminodiphenylmethane, both resins showed excellent flame retardancy with UL-94 V0 rating and high LOI value of 31.4% (coupling with DDM) and 32.8% (coupling with PDA), due to their outstanding intumescent and dense

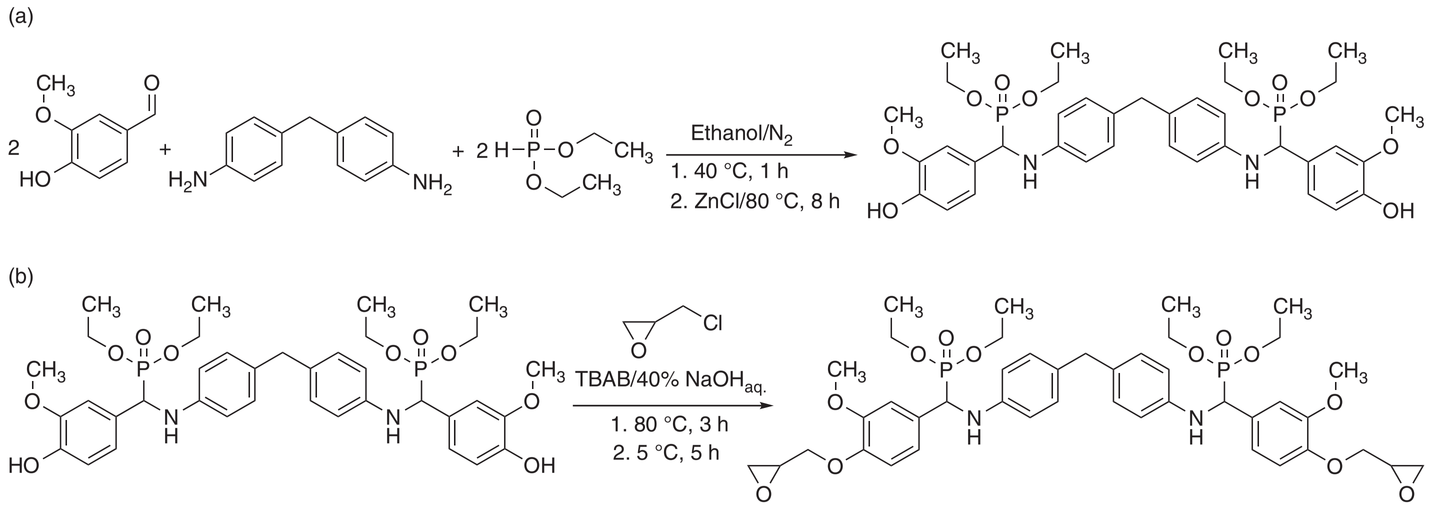


Figure 1.29 Synthesis of the vanillin coupling product (a) and the flame-retardant epoxy resin based on it (b).

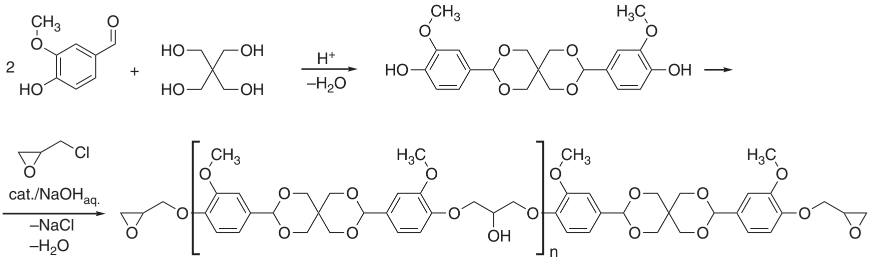


Figure 1.30 The coupling of vanillin with pentaerythritol and synthesis of the epoxy resins containing spiro-ring structure.

char formation ability. They also exhibit high glass transition temperature value of 183 °C (DDM) and 214 °C (PDA), the tensile strength of 80.3 MPa (DDM) and 60.6 MPa (PDA), and the tensile modulus of 2114 MPa (DDM) and 2709 MPa (PDA), much higher than the cured bisphenol A-based epoxy resin with a T_g of 166 °C, a tensile strength of 76.4 MPa, and a tensile modulus of 1893 MPa, respectively.

Two molecules of vanillin can also be coupled through the dehydration condensation with pentaerythritol, leading to obtain the bisphenol with the specific spiro-ring structure (Figure 1.30) [66], which can be further reacted with epichlorohydrin to give the epoxy resin.

This vanillin-based resin exhibits very interesting properties [107]. This solid resin with an epoxy value of 0.355 mol/100 g, cross-linked with diamine hardeners, DDM or 3,9-bis(3-aminopropyl)-2,4,8,10-tetroxaspiro(5,5)undecane, has several relaxations. The first is the β-relaxation, caused by the micro-Brownian motion of the aromatic methoxy group, observed from 50 to 100 °C for the spiro-ring-type resin systems in both mechanical and dielectric measurements. The peak height and the activation energy of this relaxation are independent of the degree of curing. The second one is the relaxation caused by the hydrogen bonding between the methoxy and the hydroxyl groups at around 0 °C [108]. This relaxation behavior is expected to have a positive effect on the damping characteristics. Moreover, the fracture toughness of the spiro-ring-type epoxide resin with methoxy branches is considerably greater above the temperature region of the β-relaxation than that of the bisphenol A type resin [109].

1.3.3 Cardanol

Cardanol is extracted from the shell of the cashew nut. Cashew nut comes from the cashew tree, *Anacardium occidentale*, mostly grown in India, East Africa, and Brazil [110]. The nut has a shell of about 1/8 in. thickness inside, which is characterized by a soft honey comb structure containing a dark brown viscous liquid, called cashew nut shell liquid (CNSL). Nut shells, depending on the extraction method used, contain about 30 wt% CNSL. The world production of CNSL is about one million tonnes annually [111]. CNSL is extracted from nuts using hot oil process; roasting process using solvents such as benzene, toluene, and

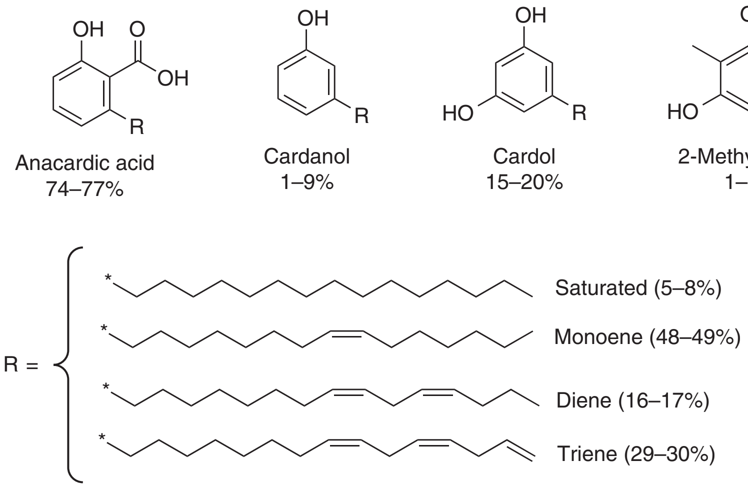


Figure 1.31 Schematic illustration of components of CNSL.

petroleum hydrocarbon; or supercritical extraction of oil using a mixture of CO_2 and isopropyl alcohol [112].

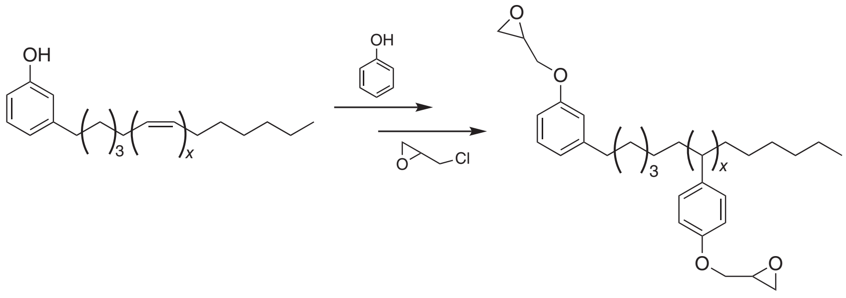
CNSL is a large and relatively cheap source of naturally occurring phenols [110]. The crude CNSL contains different long-chain phenols such as anacardic acid (3-*n*-pentadecylsalicylicacid), cardanol (3-*n*-pentadecylphenol), cardol (5-*n*-pentadecylresorcinol), and 2-methylcardol (2-methyl-5-*n*-pentadecylresorcinol) (Figure 1.31) [113].

There are various methods of purifying technical CNSL. Among them, it is worth mentioning two methods (i) column chromatography of CNSL and (ii) the method based on the formation of an amine-cardol and distillation of cardanol under high vacuum [114]. Cardanol of industrial grade is obtained throughout the thermal treatment of CNSL, followed by distillation. During that process, the decarboxylation of anacardic acid occurs, resulting in cardanol (about 90% purity) and a small quantity of cardol and methylcardol [114]. The diepoxidized cardanol (NC-514, Cardolite Corporation), obtained in a two-step process (Figure 1.32) of phenolation of aliphatic chain and then the reaction of phenol hydroxyl groups with epichlorohydrin in basic conditions, with $ZnCl_2$, at 95 °C, is an example of commercially available cardanol [115, 116].

Cardanol is a nonedible by-product of CNSL industry, and it is known as a promising aromatic renewable source, which is available in large scale. It is a yellow liquid composed of four meta-alkyl phenols differing by the unsaturation degree of aliphatic chain: 8.4% saturated, 48.5% monoolefinic (8), 16.8% diolefinic (8,11), and 29.3% triolefinic (8,11,14).

The presence of long aliphatic alkyl chain in the *meta*-position of the phenolic ring within the cardanol molecule is responsible for attractive properties such as good processability and high solubility in organic solvents, but it also influences many chemical transformations (Figures 1.33 and 1.34).

Cardanol is used as an interesting substitute to bisphenol A. For instance, cardanol-based epoxy resin is synthesized and tested as a replacement of



Diepoxidized cardanol, NC-514

Figure 1.32 Synthesis of NC-514.

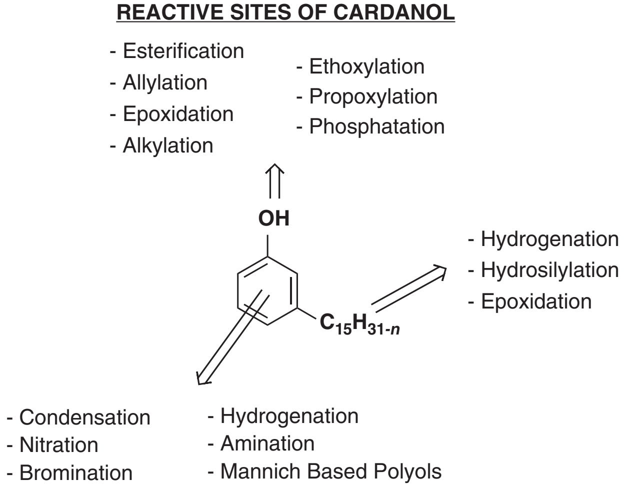


Figure 1.33 Reactive sides of cardanol.

BPA-based epoxy in coating applications [117]. The triglycidyl resin (TGC) is obtained from acetyl cardanol via a two-step reaction (Figure 1.35).

In the first step, the acetyl cardanol molecule is modified with maleic anhydride, followed by hydrolysis of the anhydride ring to prepare carboxyl functional cardanol (CFC). In the second step, the CFC reacts with excess of epichlorohydrin to prepare TGC. During that synthesis, various reactions occur: (i) grafting of maleic anhydride moiety on the aliphatic chain facilitated by hydrogen transfer, (ii) thermal rearrangements of the nonconjugated double bonds, resulting in the formation of conjugated double bonds, (iii) Diels–Alder reaction of newly created conjugated double bonds with maleic anhydride forming a Chroman ring, (iv) addition reaction by proton transfer mechanism of cardanol double bonds, and (v) radical polymerization of the double bonds resulting in a polymeric structure.

Further, the prepared TGC is used as a binder in combination with the BPA-based epoxy at various weight ratios (formulations containing 40–90% of TGC on mass basis), and it is cured with different amine hardeners: isophorone diamine (cycloaliphatic amine), 4,9-dioxadodecane-1,12-diamine (long chain

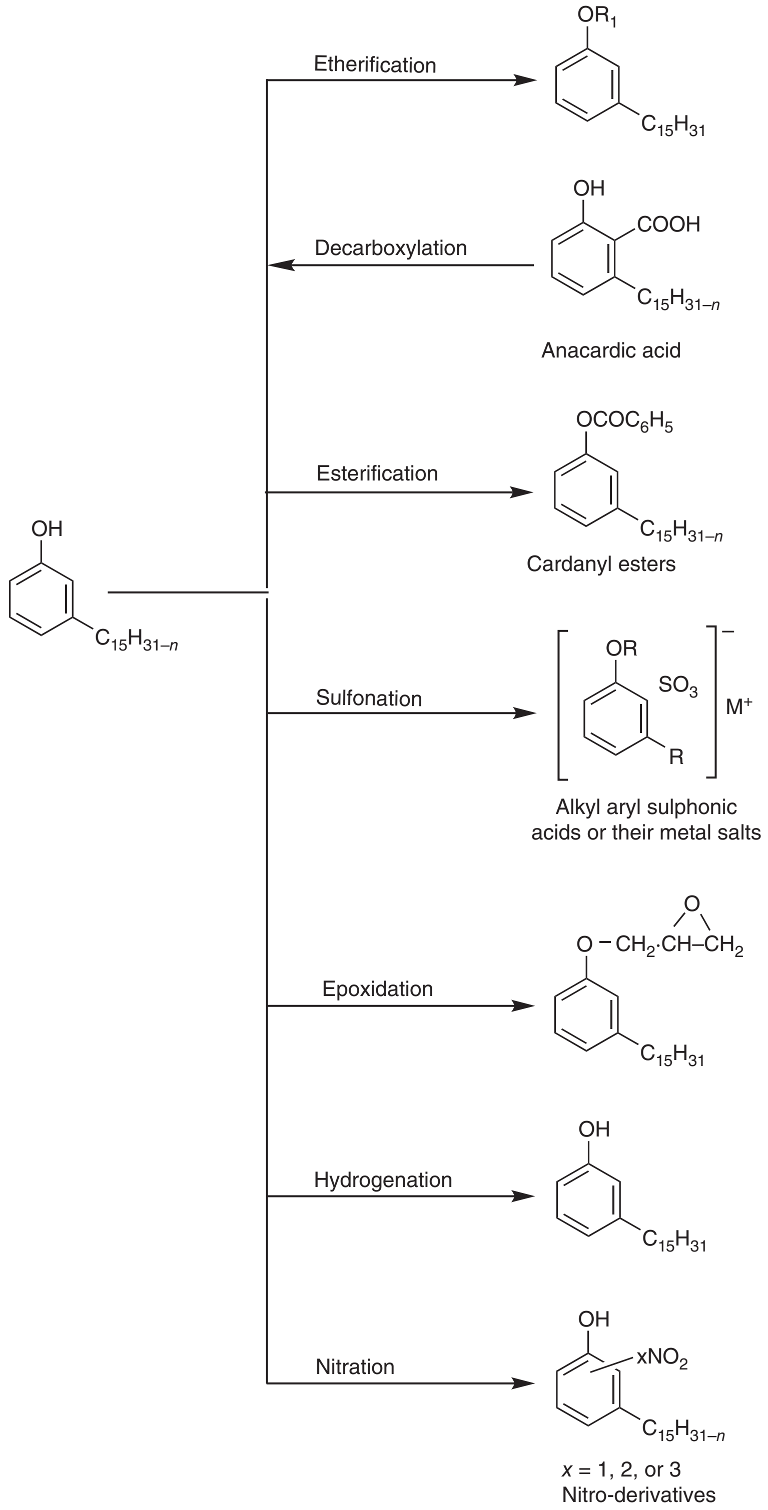


Figure 1.34 Chemical transformation of cardanol.

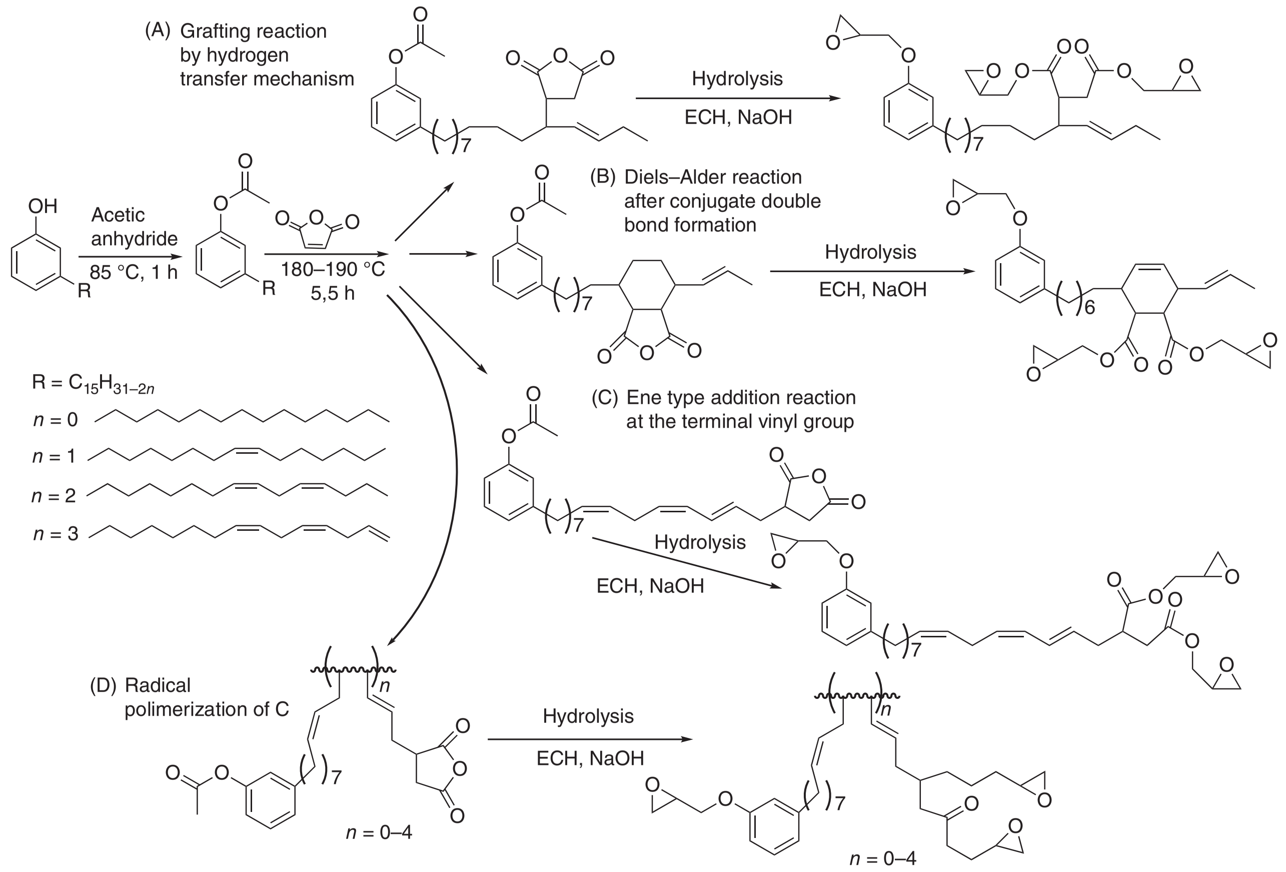


Figure 1.35 Synthesis of carboxyl functional cardanol and structures of the glycidyl products formed via the reaction of CFC and epichlorohydrin.

amine), and Replamide 325 (polymeric amine). Samples containing 40–60 wt% of DGEBA are characterized by comparable properties to that of completely DGEBA-based system, resulting from a good balance between soft and hard segments in the cross-linked structure. Additionally, the coatings with TGC are characterized by slightly lower thermal stability at higher temperatures than DGEBA-based system ($T_{10\%} = 340\,°\mathrm{C}$, while for the coatings containing TGC, $T_{10\%} = 280\,°\mathrm{C}$). The aromatic content in the case of DGEBA is higher than TGC and hence gives relatively higher thermal stability of tested samples.

NC-514, a mix of polymers of epoxidized cardanol (Figure 1.36), is used to obtain cardanol-based materials [114].

In order to synthesize epoxy networks, epoxidized cardanol is reacted with isophorone diamine and Jeffamine D400 diamine. Mass loss temperatures of cardanol networks are slightly lower than the DGEBA-based material. Additionally, the polymers synthesized from epoxidized cardanol NC-514 and IPDA exhibit lower T_g values, between 41 and 50 °C (T_g = 158 °C for DGEBA/IPDA 1 : 1, respectively). Moreover, the cross-linking density of NC-514/IPDA and NC-514/Jeff400 is almost five times lower than the cross-linking density of DGEBA/IPDA. The decrease of cross-linking density, in comparison to DGEBA, is correlated with the presence of long aliphatic chain within the structure of NC-514, which increases the distance between the epoxy groups.

In order to replace bisphenol A in epoxy networks, the application of bio-based saccharides (sorbitol and isosorbide) as epoxidized reactants in epoxidized cardanol-based resins is an interesting approach for achieving higher thermomechanical properties of cardanol-based materials [118]. Several mixtures of diglycidyl ether of cardanol NC-514 (EEW = 400 g/eq.) at different ratios (100, 75, 50, and 25 wt%) with various epoxy reactants, polyglycidyl ether of sorbitol Denacol EX622 (EEW = 188 g/eq.), and two epoxy reactants of isosorbide, Denacol GSR100 (EEW = 155 g/eq.) and Denacol GSR102 (EEW = 158 g/eq.) (Figure 1.37), are cured at room temperature with two commercial amines: trifunctional polyetheramine (Jeffamine T403) and isophorone diamine (Aradur 42BD).

Based on the results, it was stated that even if epoxidized cardanol-based networks cannot fully replace DGEBA materials, the combinations of epoxy cardanol with other bio-based epoxy reactants can alter the thermomechanical properties of cardanol-based networks. The obtained materials are characterized by properties comparable to bisphenol A-based materials. T_g and hardness in Shore A scale of samples of epoxidized sorbitol-cardanol at a 1 : 1 weight ratio are higher than that of the same ratio of epoxidized isosorbide (60 °C and 93 as compared to 48 °C and 91). Material based on epoxidized isosorbide-cardanol (3 : 1) exhibits T_g of 83 °C (isosorbide 100, with EEW = 155 g/eq.) and 62 °C (isosorbide 102 with EEW = 158 g/eq.), respectively.

Moreover, cardanol derivative obtained throughout the reaction of cardanol with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (Figure 1.38) might be used as the flame-retardant agent [119].

A triscardanyl phosphate (PTCP) containing phosphaphenanthrene groups is synthesized via dehydrochlorination, epoxidation, and ring opening reaction of cardanol (Figure 1.39).

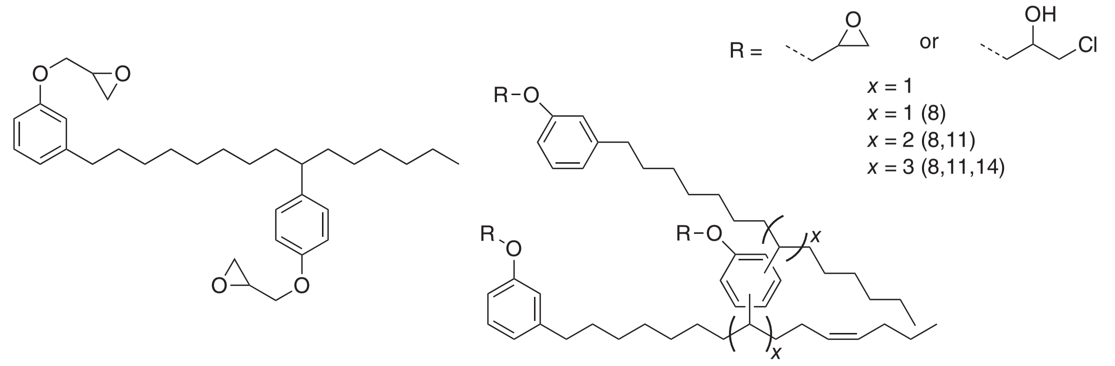
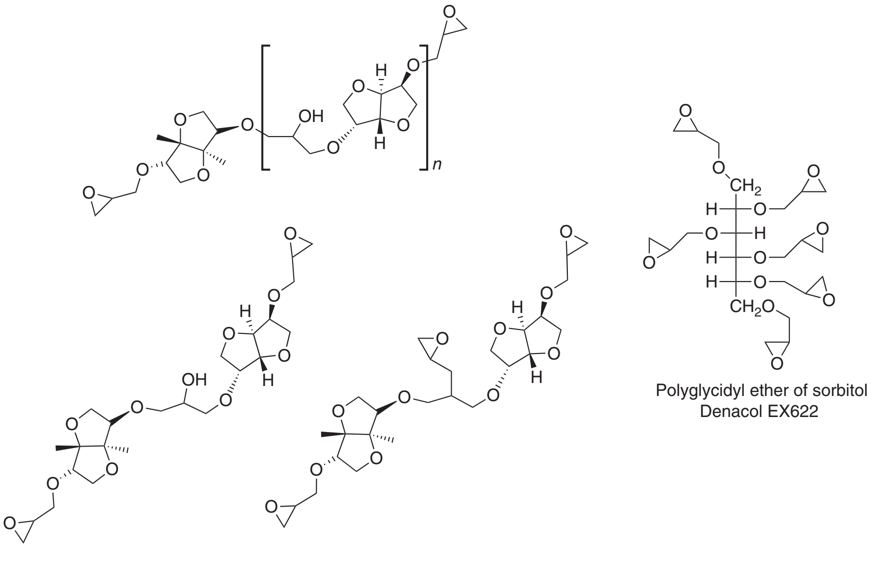


Figure 1.36 Chemical structure of cardanol NC-514.

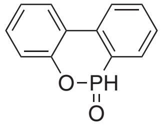


Possible structures of epoxidized isosorbide

Polyglycidyl ether of sorbitol
Denacol EX622

Figure 1.37 Epoxy reactants: epoxidized isosorbide and polyglycidyl ether of sorbitol.

Figure 1.38 Chemical structure of DOPO.



9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

Based on the performed studies (Table 1.5), it was observed that the incorporation of PTCP into DGEBA epoxy resin accelerates the thermal degradation process and improves the char yield.

The same higher char yield is valuable toward improving the flame-retardant properties of epoxy resins. The LOI value of EP/PTCP-30% increases from 23.0% (neat epoxy material) to 30.5%. Moreover, compared with neat epoxy resin, the impact strength of EP/PTCP-30% increases by 29%.

Cardanol is an interesting nonedible by-product of CNSL industry. Because of the presence of phenolic hydroxyl group, olefinic linkages in the alkyl chain, and aromatic ring, it is a promising nonharmful renewable substituent to BPA. The presence of long aliphatic chain of cardanol in bio-based epoxy resins results in lower T_g values of obtained materials than those with DGEBA. At the same time, these materials are characterized by very interesting thermal stabilities. Moreover, the mechanical properties of cardanol-based epoxies are lower than DGEBA epoxies. However, numerous, described in the literature, studies tested coating applications of epoxies obtained with the cardanol derivatives.

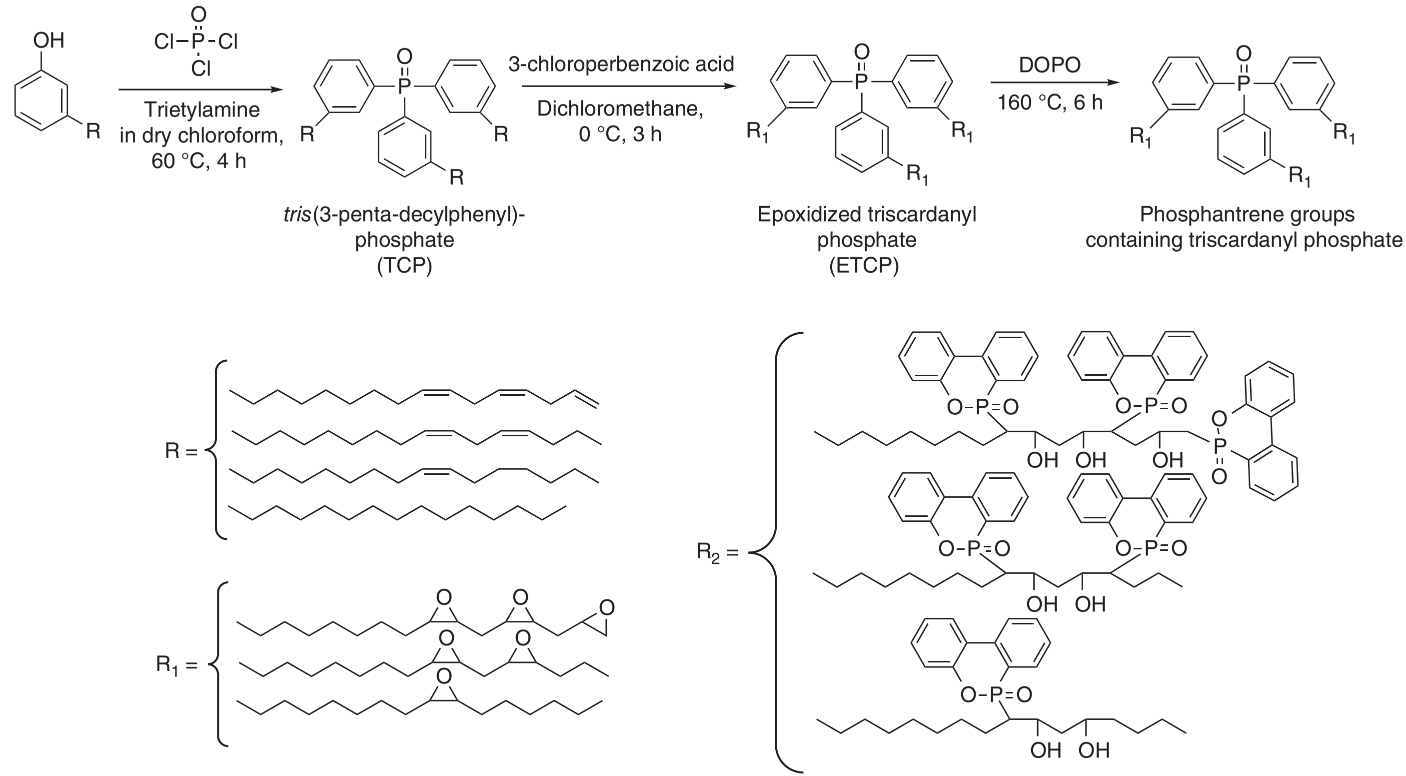


Figure 1.39 Synthesis of PTCP.

Table 1.5 Thermal and mechanical properties of PTCP, neat epoxy, and EP/PTCP samples.

Sample	Thermal properties					Mechanical properties			
	$T_{10\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char residue (%)	LOI (%)	Impact strength (kJ/m^2)	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PTCP	286	322	500	2.8	—	—	—	—	—
EP	361	367	554	1.4	23.0	14.9 ± 1.1	1.56 ± 0.10	40.6 ± 2.5	2.2 ± 0.8
EP/PTCP-10%	336	344	554	4.2	26.5	16.8 ± 1.0	1.35 ± 0.00	46.3 ± 3.4	5.5 ± 01
EP/PTCP-20%	328	344	575	5.7	28.0	18.1 ± 1.4	1.46 ± 0.03	60.8 ± 4.4	7.7 ± 1.8
EP/PTCP-30%	311	335	577	8.3	30.5	19.1 ± 0.5	1.09 ± 0.09	46.7 ± 1.1	8.2 ± 0.4

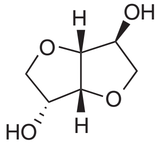


Figure 1.40 Chemical structures of isosorbide.

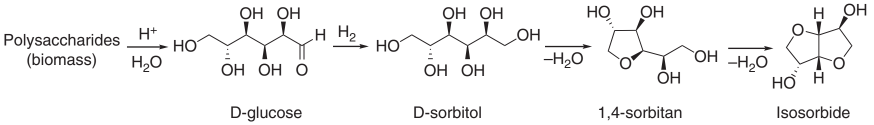


Figure 1.41 Schematic reaction pathway for the production of bio-based isosorbide.

1.3.4 Isosorbide

Isosorbide (1,4:3,6-dianhydro-D-glucitol) is an organic oxygen-containing heterocyclic compound composed of two fused furan rings (Figure 1.40).

Isosorbide does not occur naturally. It can be obtained from various raw materials by organic synthesis through different reaction pathways. However, nowadays, isosorbide is produced from diverse polysaccharides through the multistep process that includes several intermediates [120] (Figure 1.41).

The synthesis of isosorbide can start from polysaccharides (mainly starch or cellulose biomass) or directly from all of the intermediate compounds because they are currently commercially available on a large scale. Lignocellulosic biomass is considered as one of the best resource due to its abundancy, versatility, and price [121]. The synthetic process of isosorbide production from polysaccharides consists of the following stages: acid-catalyzed hydrolysis of the glycosidic bonds in the polymeric carbohydrates, hydrogenation of obtained glucose to sorbitol and further dehydration to sorbitan, and finally dehydration of sorbitan to isosorbide. Moreover, the different side reactions (such as degradation or polymerization) can occur in this complex process. Therefore, different new synthesis strategies (including the one-step synthesis from glucose and cellulose) and catalysts are still elaborated and proposed [122].

Isosorbide can be derivatized by functionalization or substitution of the two secondary hydroxyl groups present in its molecule. A certain difficulty is the different reactivity and steric hindrance of the hydroxyl groups (against, due to these, a selective monoderivatization is also possible). Nevertheless, isosorbide is currently converted to valuable derivatives for use as pharmaceuticals, detergents, emulsifiers for cosmetics, surfactants, stabilizers, or plasticizers. In addition to the above-mentioned applications, for a long time, isosorbide is considered and intensively studied as a potential monomer building block for the biopolymeric materials (e.g. polycarbonates, polyurethanes, or polyesters). As the bio-based diol with bicyclic rigid structure isosorbide can also be applied as a substitute for bisphenol A replacement, there are generally two ways for introducing an epoxy functionality into the isosorbide molecule (Figure 1.42): conversion to the diallylic derivative, followed by oxidation to oxirane rings (the first pathway) and reaction with epichlorohydrin (the second and third pathways).

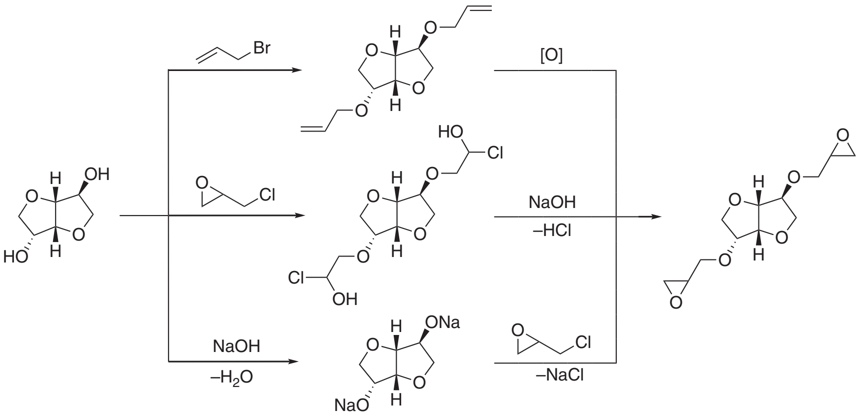
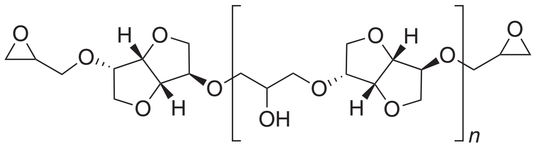


Figure 1.42 Possible reaction pathways for the synthesis of the diepoxide derivative of isosorbide.

Figure 1.43 Structure of isosorbide-based epoxy resins.



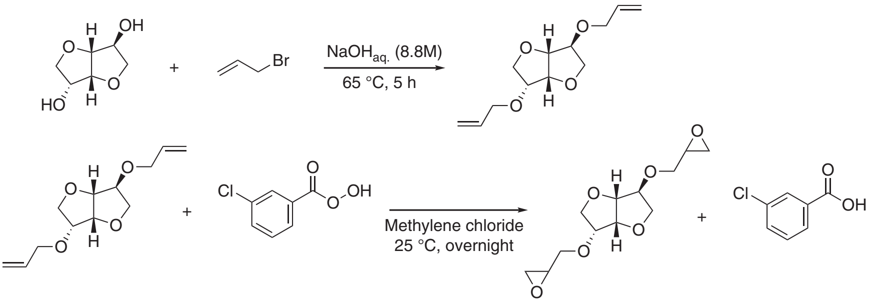


Figure 1.44 Synthetic route of diallyl isosorbide and isosorbide diglycidyl ether.

In fact, the chemical structure of the diglycidyl isosorbide derivative shown in Figure 1.42 is valid only for the first reaction pathway. Only by the reaction with allyl bromide, followed by oxidation of the terminal unsaturated bonds, it is possible to obtain the product containing only one isosorbide molecule (the monomer). For the remaining reaction pathways, even the use of a large excess of epichlorohydrin leads to the formation of the products with an oligomer structure (Figure 1.43).

According to the first reaction pathway, the diallyl ether can be prepared by heating the isosorbide with allyl bromide in sodium hydroxide solution (Figure 1.44) [123].

Oxidation of diallyl isosorbide ether to isosorbide diglycidyl ether is carried out in the reaction with *meta*-chloroperbenzoic acid as an oxygen carrier. It is also possible to use 4-allyoxybenzoly chloride to introduce the diallyl functionality (Figure 1.45) [124].

The next stage of the reaction is carried out using the *meta*-chloroperbenzoic acid, as described above.

The synthesis of isosorbide-based epoxy resins using epichlorohydrin (Figure 1.43) can be accomplished in a different manner. Isosorbide can be reacted with a large excess (even a 10-fold) of epichlorohydrin in the presence of strong alkali–sodium hydroxide (40% aq. solution) in a single-stage reactor with continuous removal of water [125]. The reaction is carried out at a temperature of 109–115 °C for eight hours and the product with an epoxy value of 0.451–0.467 mol/100 g is obtained. In another method, sodium hydride as a base in diglyme is used to prepare the disodium salt of isosorbide (reaction time about six hours at a temperature of 43–48 °C and then one hour at a temperature of 85 °C) [126], which is then reacted with nearly 20-fold excess of epichlorohydrin (six hours of dropwise addition, leaving overnight at room temperature, and heating for 2.5 hours at a temperature of 55 °C). The resulted product is obtained with an epoxy value of 0.359 mol/100 g. Sodium hydroxide (50% aq. solution) can be used instead of sodium hydride [127], also in the two-step method. The disodium salt of isosorbide synthesis is catalyzed by trimethylcetylammonium bromide. In the second step, the disodium salt is reacted with the 10-fold excess of epichlorohydrin in the presence of another phase transfer catalyst – tetrabutylammonium bromide (heating at a temperature of 115 °C for about three hours is carried out). The obtained isosorbide-based epoxy resin has an epoxy value of 0.518 mol/100 g.

It is also possible to react isosorbide with epichlorohydrin in a two-stage process under different conditions [128]: using an aqueous alkali (mostly sodium/potassium hydroxide) and an organic solvent (toluene and dimethyl acetamide) or the first stage is carried out in the presence of the Lewis acid catalyst (stannous fluoride).

The cross-linked bio-based epoxy resin (an epoxy value of 0.440 mol/100 g), synthesized in the one-step reaction from isosorbide and epichlorohydrin [129] in the presence of 50% aqueous NaOH, exhibits properties comparable to those of the commercial bisphenol A-based resin Epidian 5 (an epoxy value of 0.510 mol/100 g). Depending on the cross-linking agent used (triethylenetetramine, isophoronediamine, tetrahydrophthalic, and phthalic anhydrides), the selected mechanical properties of the isosorbide-based resin are in some cases even better (the flexural and compression strengths and the Brinell hardness). Also, the Izod impact strength of this resin is usually better than that of the cross-linked resin Epidian 5 (even more than four times). Water sorption of the isosorbide-based resin is much higher than that of the bisphenol-A-based resin (for the sample cross-linked with triethylenetetramine, even their disintegration is observed), and as a result, the chemical resistance is less than that for the resin Epidian 5.

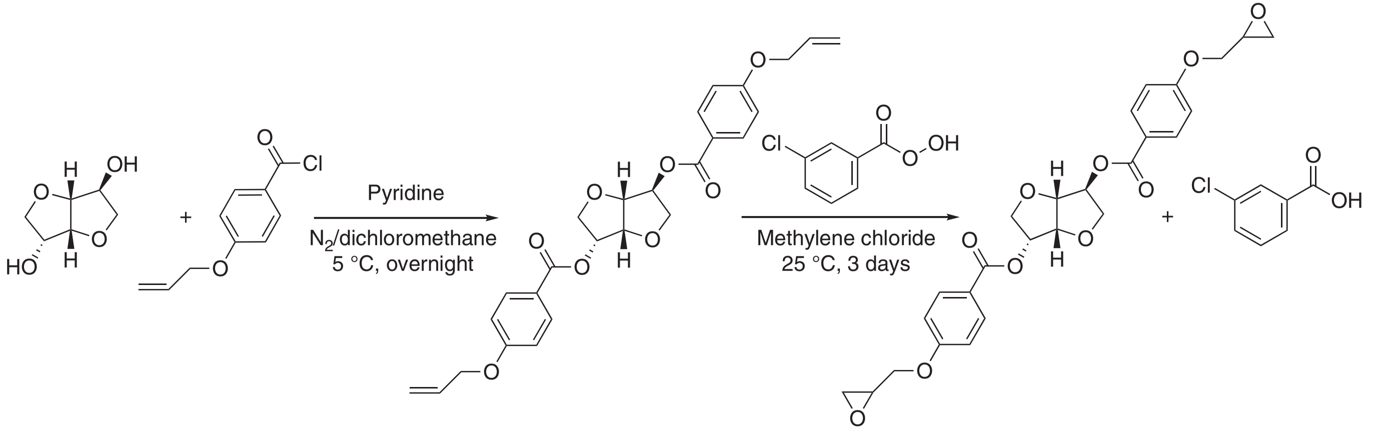


Figure 1.45 Synthesis of isosorbide diglycidyl ether using 4-allyoxybenzoly chloride.

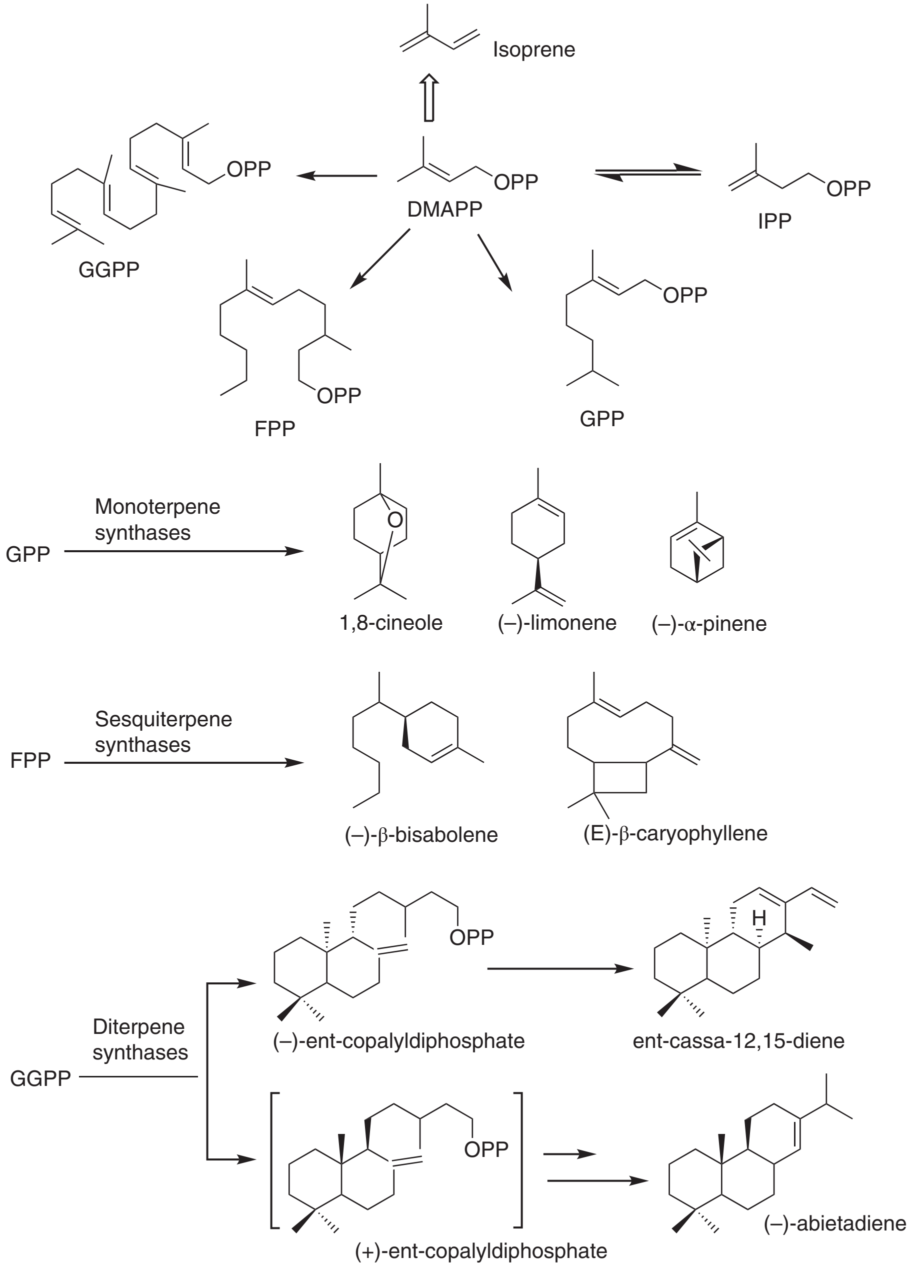


Figure 1.46 Formation of plant terpenes.

1.3.5 Terpene Derivatives

Terpenes and terpenoids are an interesting group of natural resources, with relatively large potentials as substrates for the synthesis of various polymers. They are unsaturated aliphatic structures, predominantly derived from turpentine, the volatile fraction of resins exuded from conifers [130]. The C5-units of isopentenyl diphosphate (IPP) and its isomer dimethylallyl diphosphate (DMAPP) are the initial substrates for the synthesis of terpenes. It is worth highlighting here that the linear prenyl diphosphates: geranyl diphosphate (GPP, C10), farnesyl diphosphate (FPP, C15), and geranylgeranyl diphosphate (GGPP, C20) are precursors of terpenes obtained via the biosynthesis in the presence of prenyltransferases (Figure 1.46). Due to the fact that terpenes consist of multiple isoprene units (C_5H_8, 2-methyl-1,4-butadiene), they are categorized based on the number of units into hemiterpene (one isoprene unit, C5), monoterpene (two units, C10), sesquiterpene (two units, C15), diterpene (four units, C20), and so on [131] (Figure 1.46) [132].

Terpenes are built from a wide range of cycloaliphatic and hydrocarbon chain structures with repeating isoprenyl double bonds. Terpenoids can be viewed as modified terpenes with added, missing, or shifted methyl and oxygenated functional groups (Figure 1.47).

The global turpentine production is more than 300 000 tons per year, and it includes α-pinene (45–97%) and β-pinene (0.5–28%), with smaller amounts of other monoterpenes [130]. The pinenes and limonenes are natural chemical precursors to a wide variety of compounds used in the pharmaceutical, fragrance, and flavor industry. Pinenes, additionally, are a source of other less common terpenes (Figure 1.48).

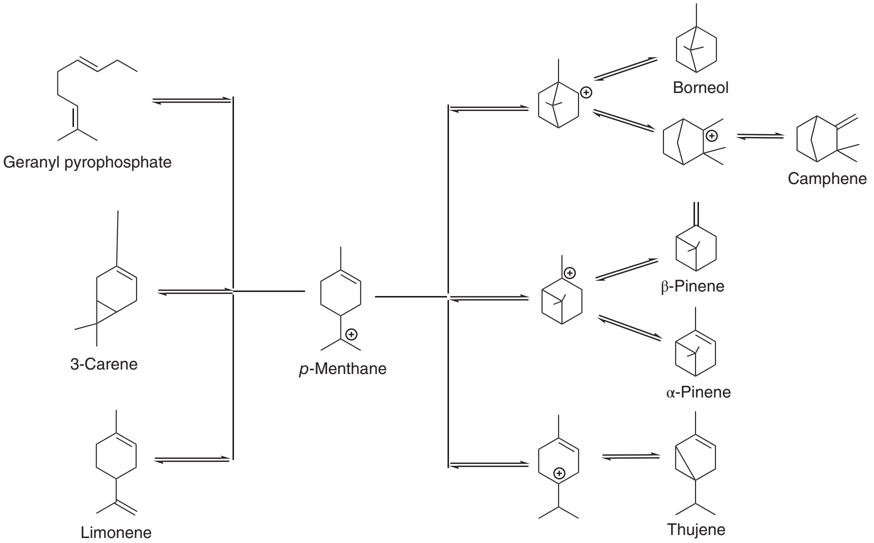


Figure 1.47 Outline of the biosynthetic pathway leading to the major monoterpenes from a single precursor.

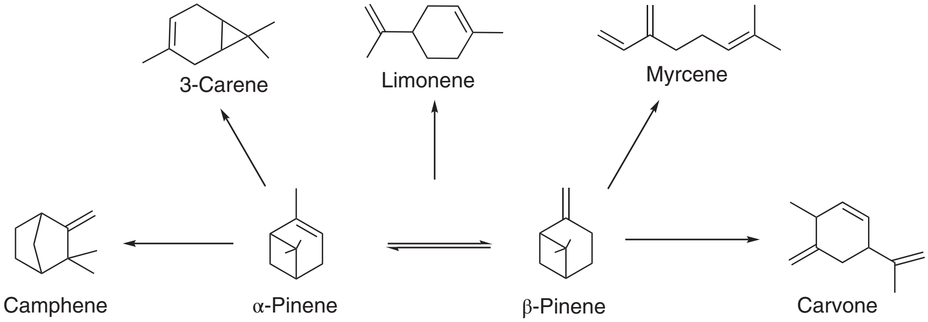


Figure 1.48 Isomerization and oxidation processes for converting pinenes into other terpenes and a terpenoid.

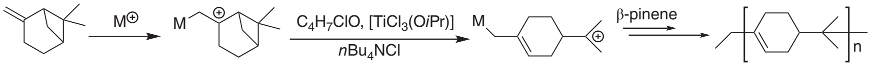
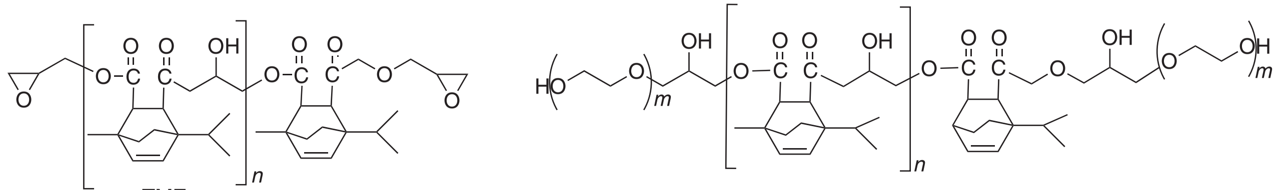


Figure 1.49 Mechanism of the cationic polymerization of β-pinene.

A methyl group or other electron-donating groups on the double bond present within the structure of compounds obtained via the isomerization and oxidation of pinenes makes them susceptible for cationic polymerization. However, because of the presence of highly reactive *exo*-methylene double bond within the β-pinene structure, most of the polymerization reactions involve β-pinene, not α-pinene (Figure 1.49).

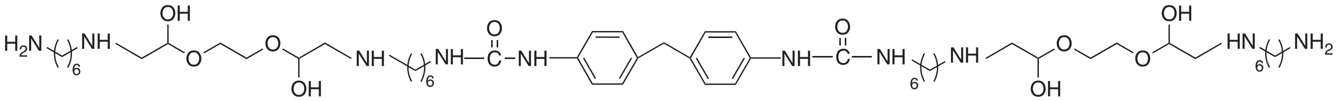
Some cationic polymerization of terpenes leads to oligomers or low molecular weight polymers, which along with other terpene monomers might be used for the synthesis of epoxy resins. One of the interesting applications of terpenes is the synthesis of hydrogenated terpinene-maleic ester type epoxy resin [133]. A bio-based epoxy resin (denoted as TME) and a waterborne dispersion of TME (denoted as WTME) obtained from the turpentine (Figure 1.50) are nontoxic alicyclic structure epoxy resins without BPA.

The resulting film with good thermal stability and antifouling properties is transparent and flexible. However, because the obtained cured terpene-based products are characterized by worse mechanical properties than those of BPA-based epoxy resin, two different approaches had also been studied: (i) incorporation of cellulose nanowhiskers (CNWs) suspension, hydrolyzed from microcrystalline cellulose [134], and (ii) in combination with polyurethane [133]. In the first modification of the synthesis, the incorporation of CNWs in the WTME matrix (0.5–8 wt%) results in the increase of the storage modulus at 150 °C (from 0.8834 to 4.756 MPa), Young's modulus (from 295.6 to 800.1 MPa), and tensile strength (from 7.08 to 15.2 MPa) compared to unmodified WTME. Noted improved properties might be attributed to the formation and increase of interfacial interaction by hydrogen bonds between CNWs nanofiller and the WTME matrix. On the other hand, in the second approach (Figure 1.51), an anionic polyol (T-PABA) dispersion is prepared by modifying terpene-based epoxy resin with *para*-aminobenzoic acid and then cross-linked



TME

TME-based emulsifier



Hydrophilically modified aliphatic amine

Figure 1.50 Chemical structures of TME, TME-based emulsifier, and aliphatic amine.

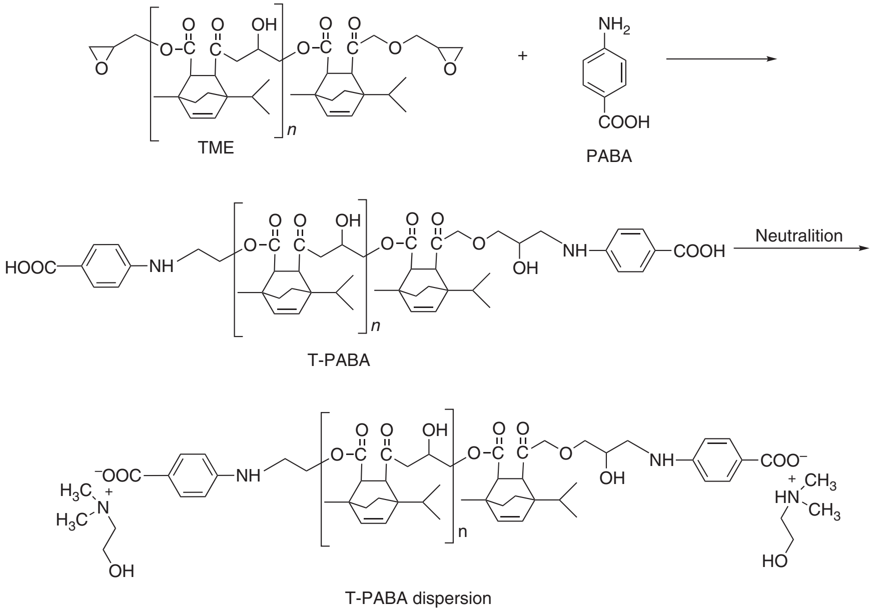


Figure 1.51 Preparation of T-PABA and T-PABA dispersion.

with a hexamethylene diisocyanate (HDI) tripolymer to prepare waterborne polyurethane/epoxy resin composite coating. These new cross-linked products combine the rigidity and weatherability of the saturated terpinene alicyclic epoxy resin with the flexibility and tenacity of the polyurethane.

On the other hand, the oxidation of limonene, the terpene derivative, which within the structure contains two double bonds, (i) vinylene group allocated in the ring and (ii) vinylidene side group, results in limonene monoepoxide and diepoxide – compounds commercially applied as reactive diluents in epoxy applications [135]. Additionally, D-limonene might also be used in the synthesis of epoxy resins as a bio-based replacement for conventional DGEBA resins [136]. Hybrid epoxy resin, including naphthalene and limonene moieties, is obtained on the course of the three-step reaction (Figure 1.52) consisting of (i) alkylation of naphthol with limonene in the presence of Friedel–Crafts catalyst, (ii) introduction of methylene linkage between naphthalene rings to obtain product **2** with higher molecular weight, and subsequently (iii) epoxidation of **2** with epichlorohydrin in the presence of sodium hydroxide and polyethylene glycol to give epoxy resin **3**.

The obtained epoxy resin is mixed with dicyanodiamide and a bisphenol A formaldehyde novolac resin used as curing agents in a molar stoichiometric ratio of 1 : 1 and in the presence of 2-methylimidazole as an accelerator. Compared to DGEBA resins, the cured D-limonene/naphthol-based epoxy resins are characterized by higher T_g (by 75 °C) and thermal stability with higher temperatures of maximum rate of weight loss in air by about 40 °C.

Epoxy resins might also be synthesized from rosin, produced by heating fresh tree resin to remove the volatile liquid terpenes [137]. Because of the presence of

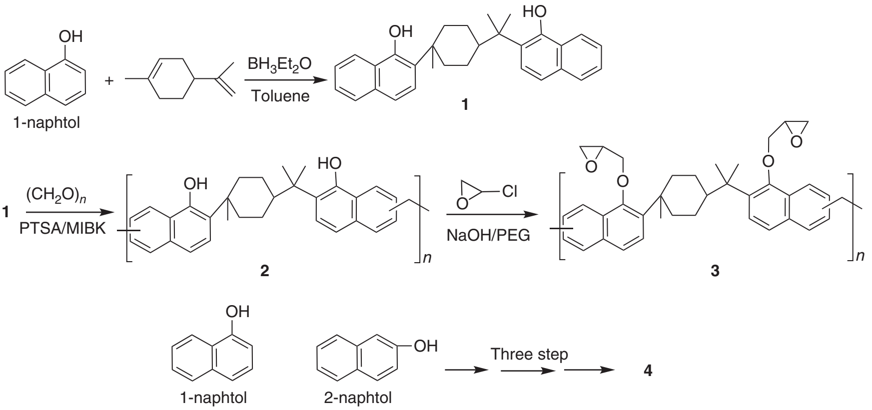


Figure 1.52 Synthesis of epoxy resins starting from naphthol and limonene.

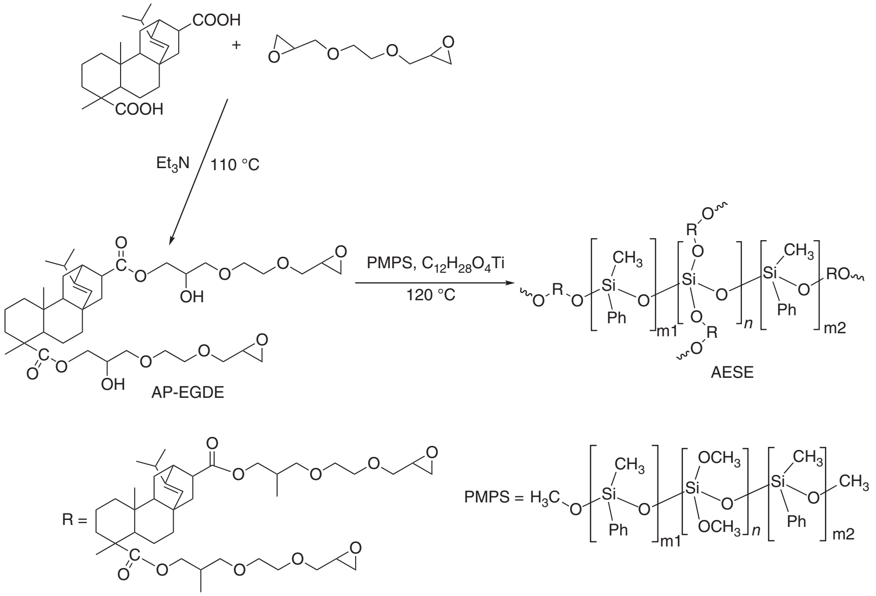


Figure 1.53 Synthetic route to a rosin-based siloxane epoxy monomer (AESE).

rigid hydrogenated phenanthrene ring in the molecular structure, rosin is suitable as an alternative to DGEBA [138, 139]. The interesting examples are the flame-retardant rosin-based epoxy thermosets, such as a rosin-based siloxane epoxy monomer (AESE), which is prepared by the reaction of ethylene glycol diglycidyl ether modified acrylpimaric acid (AP-EGDE) with polymethylphenylsiloxane (PMPS) (Figure 1.53) [140].

The incorporation of PMPS results in the improvement in the LOI value compared to the AP-EGDE/MHHPA thermosets. The highest LOI value of 30.2% is noted for the cured product containing 30 wt% of AESE (AESE30/MHHPA). Because of the presence of the flexible chains of the PMPS, all the AESE/MHHPA thermosets display a relatively low tensile strength (<15 MPa) but on the other hand much larger elongation at break (>50%).

Terpenes are an interesting group of raw materials that might be used in the synthesis of epoxy resins. Even though not all terpenoids contain aromatic and/or phenolic moieties, these requirements can be reached via different synthesis steps (e.g. carvacrol, for instance, might be obtained from other turpentine components, limonene, for instance, throughout an oxidation, followed by an isomerization process).

1.4 Bio-Based Epoxy Curing Agents

Cross-linking of epoxy resins takes place with the participation of oxirane rings present in them. The strained structure of these rings is the reason for their high reactivity and facilitates their opening under the influence of very different factors. Epoxy resin curing generally takes place under the influence and with the participation of multifunctional chemical compounds with active protons. These are mainly polyamines (aliphatic, aromatic, and cycloaliphatic) and carboxylic compounds (acids and anhydrides). Cross-linking of the epoxy resins can also be accomplished by a mechanism of ring-opening polymerization using suitable catalysts. This is an important method of cross-linking, especially coating materials. However, the search for compounds of natural origin, which could replace petrochemical hardeners, is the most important in the case of polyamines and carboxyl compounds that are used for cross-linking in stoichiometric ratios to the content of epoxy groups in the resin. The consumption of ring-opening polymerization catalysts is insignificant compared to the polyamine and carboxylic hardeners. Usually, they are used in an amount of up to several percents by weight relative to the weight of the cross-linked resin. Therefore, new biohardeners should be sought first and foremost among the compounds of natural origin with amine or carboxylic functionalities. The appropriate reactivity and adequate miscibility with epoxy resins are the conditions, which are limiting the use of these new compounds.

Considering the possibilities of using plant oils as raw materials for the synthesis or modification of epoxy resins, an interesting solution would be just to give the plant oils proper functionality so that they can also act as natural hardeners. The use of modified vegetable oils in this role is favored by their very good miscibility with the epoxidized vegetable oils and good miscibility with the epoxy resins based on bisphenol A (despite the differences in the polarity of both groups of materials). For example, hydrolyzed castor oil can serve as a source of dehydrated fatty acids from which reactive polyamides are obtained by reaction with acrylic acid [141] (Figure 1.54) and then with various polyamines (diethylenetriamine, triethylenetetramine, and tetraethylenepentamine) [17].

The obtained polyamides (with amine values from 310 to 389 mg KOH/g) can be used to cross-link the epoxy resins based on bisphenol A giving the materials with good coating properties.

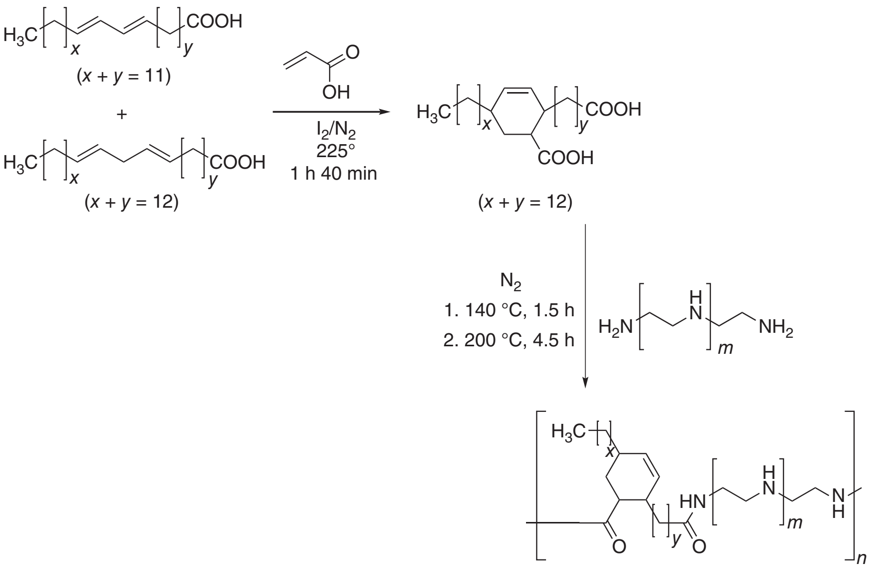


Figure 1.54 Synthesis of C_{21} cycloaliphatic dicarboxylic acids and reactive polyamides from them.

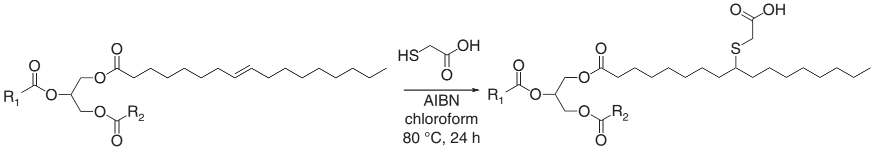


Figure 1.55 Scheme of soybean oil functionalization with thioglycolic acid.

Vegetable oil-based curing agents can be obtained through direct oil modification. The novel bio-based polyacid hardener is synthesized by the thiol-ene coupling of soybean oil with thioglycolic acid (Figure 1.55) [142].

The synthesized soybean oil-based polyacid exhibit a functionality of 3.3 acid functions per triglyceride molecule. This polyacid curing agent is characterized by the high reactivity toward epoxy groups. The low molecular weight bisphenol A-based epoxy resin cross-linked with the bio-polyacid exhibits interesting properties for coating and binders (the Shore A hardness of 52 and $E' = 0.59\,\text{MPa}$). A commercially available mercaptanized soybean oil (prepared by direct addition of H_2S to soybean oil) reacted with allylamine (Figure 1.56) or its salts can also be potentially used as a cross-linking agent for epoxy resins [143].

Modified lignin derivatives are also applied as curing agents for the epoxy resins. Commercially, various curing agents for epoxy resins are available. The commonly used petroleum-based curing agents include amines, amides, hydroxyls, acid anhydrides, phenols, and polyphenols. However, recently, a great effort has been put on obtaining new bio-based hardeners for epoxy systems. Generally, lignin-based curing agents are prepared by two different methods: (i) the reaction of lignin with ozone in the presence of NaOH to give lignin with

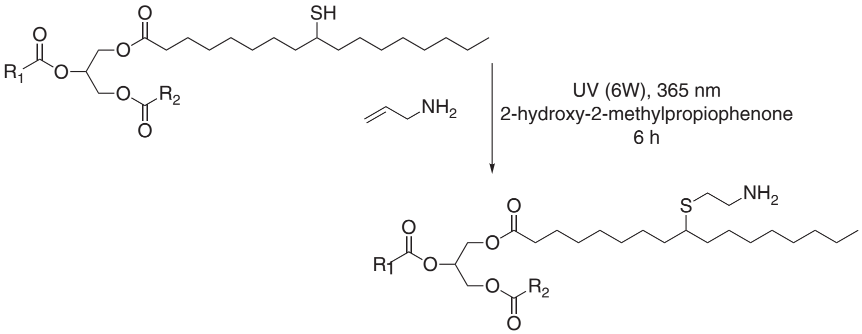


Figure 1.56 Synthesis of a polyamine cross-linking agent via thiol-ene reaction of mercaptanized soybean oil with allylamine.

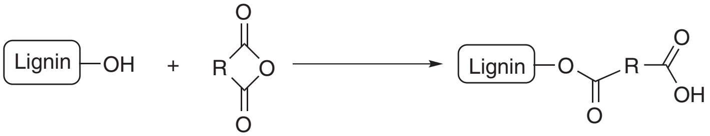


Figure 1.57 Synthesis of carboxylic acid from lignin.

unsaturated carboxyl groups (Figure 1.57) or (ii) throughout the reaction of modified lignin (partially depolymerized lignin or polyol solutions of alcoholysis lignin) with anhydrides or trimellitic anhydride chloride [144].

Another interesting approach is using aminated lignin (black powder, amine value: 180–200 mg KOH/g) as a cross-linker of bisphenol A-based epoxy resin (epoxy value: 0.48–0.54 mol/100 g) [145]. The obtained aminated lignin contains a large number of primary and secondary amine groups, which successfully cure the epoxy network (Figure 1.58).

The application of aminated lignin has the positive effect at the initial degradation stage of the epoxy resin. Because lignin itself has a good thermal–mechanical performance, samples prepared with its higher content presented accordingly improved properties (Table 1.6).

TGA and DMA tests reveal improved thermal–mechanical properties of the bio-based epoxy resin. In comparison to the epoxy resin cross-linked with the commercial curing agent based on modified isophorone diamine (W93 curing agent: amine value: 550–600 mg KOH/g), the recorded value of T_{10}, for the material cured with the hardener containing 20 wt% of aminated lignin, increased nearly by 50 °C, while the highest value of T_{10} was achieved for the epoxy system cured by 100% aminated lignin (T_{10} = 266 °C for 100% of petrochemical-based hardener W93, T_{10} = 315 °C and T_{10} = 332 °C for aminated lignin hardener, 80%W93 + 20%AL and 100%AL, respectively). Additionally, the mass loss before 300 °C of the epoxy resin cured by W93 is four times higher than the one recorded for the aminated lignin. Moreover, the obtained materials are characterized by improved values of the glass transition temperature and thermal deformation temperature. T_g and T_d of epoxy resin sample cured with

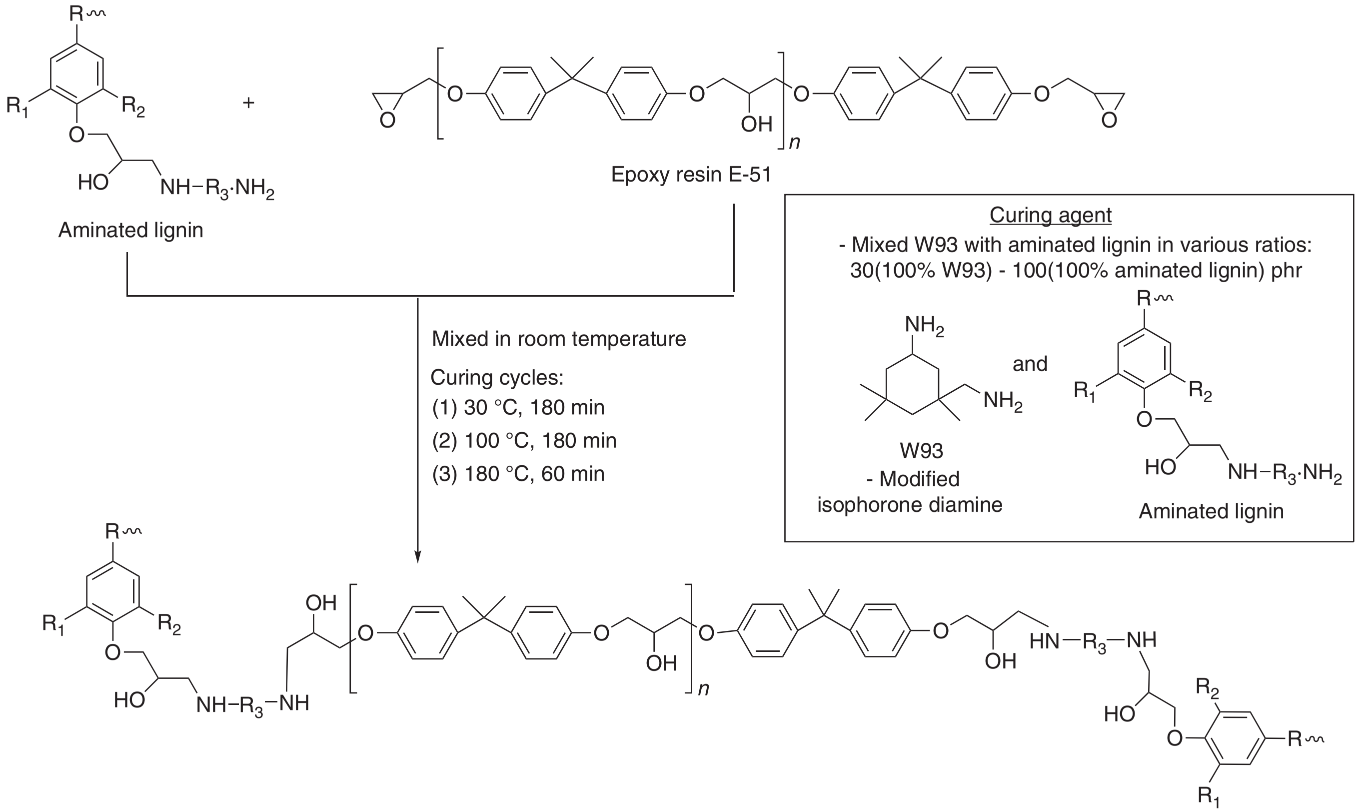


Figure 1.58 The curing of epoxy resin using aminated lignin as a curing agent.

Table 1.6 TGA, T_g, and T_d values of epoxy resin samples cured with different contents of lignin in the curing agent [145].

Epoxy resin cured by different hardeners	Total mass loss before 300 °C (%)	T_{10} (°C)	T_{50} (°C)	T_g (°C)	T_d (°C)
100%W93	11.1	266	362	79	70
80%W93 + 20%AL	8.7	315	370	86	74
70%W93 + 30%AL	—	—	—	89	76
60%W93 + 40%AL	7.2	325	364	92	79
50%W93 + 50%AL	—	—	—	93	84
40%W93 + 60%AL	8.4	317	371	—	—
20%W93 + 80%AL	5.5	327	363	—	—
100%AL	3.7	332	372	—	—

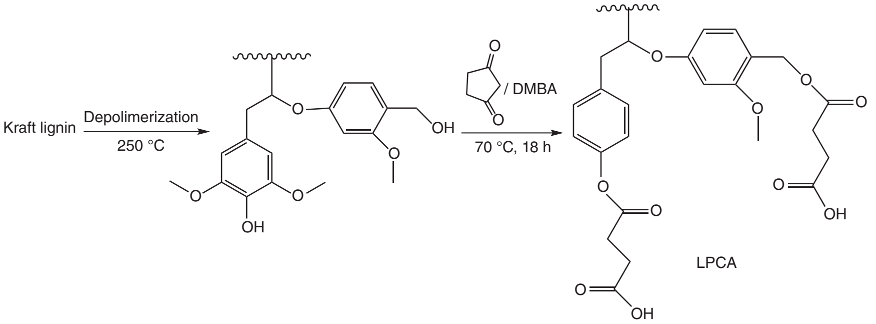


Figure 1.59 Preparation of partially depolymerized lignin (PDL) and lignin polycarboxylic acid LPCA) from Kraft lignin.

the hardener containing 50 wt% of lignin increased by 14 °C compared with the one without lignin.

Another interesting utilization of lignin-based compounds for the curing purposes of epoxy resin is application of partially depolymerized Kraft lignin [146]. In order to increase its solubility in organic solvents, lignin is subjected to the base-catalyzed depolymerization in supercritical methanol. The resulting partially depolymerized lignin (PDL) is then converted to lignin-based polycarboxylic acid (LPCA) by reacting with succinic anhydride (Figure 1.59).

LPCA might be applied as a curing or co-curing agent for epoxy resins. The curing of a commercial epoxy (DER353, epoxy value: 0.500–0.526 mol/100 g) using LPCA is conducted in the presence of 1 wt% of ethyl-4-methyl-imidazole as a catalyst and at the similar temperature range to the commercial hexahydrophthalic anhydride (HHPA). The obtained cured material exhibits a moderate T_g and comparable storage modulus to that cross-linked with a commercial anhydride curing agent. Additionally, linear succinate monoester, used in the synthesis of LPCA, enhances the flexibility of the lignin molecules. Therefore, increasing the content of bio-curing agent in the formulation tends to reduce the T_g of cured resins. For composition of DER353/LPCA with equivalent ratio 1/0.6, 1/0.8, to 1/1, the T_g of the cured resins decreases from 78.5 and 69.4 to 62.3 °C, while the storage moduli at room temperature is comparable (2.4–2.7 GPa). Based on the studies on the application of the solid LPCA together with other liquid curing agents, such as glycerol *tris*(succinate monoester) and commercial hexahydrophthalic anhydride to cure epoxies, it was observed that using a mixture of LPCA and a liquid curing agent not only adjusts the viscosity of the resin system but also significantly regulates the dynamic mechanical properties and thermal stability of the obtained epoxy materials.

Moreover, interesting two different types of novel cross-linked epoxy resins from lignin and glycerol are reported [147]. The first one is obtained by mixing the product of sodium lignosulfonate (LS) and glycerol (LSGLYPA, where the content of LSGLYPA varies at 0, 20, 40, 60, 80, and 100%) with polyacid of sodium lignosulfonate and ethylene glycol (LSEGPA) and ethylene glycol diglycidyl ether (EGDGE) at 80 °C (Figure 1.60).

The second one is by mixing LSGLYPA with a mixture of EGDGE/GLYDGE (the content of EGDGE/GLYDGE mixture was 0, 20, 40, 60, 80, and 100%) under similar reaction conditions (Figure 1.61).

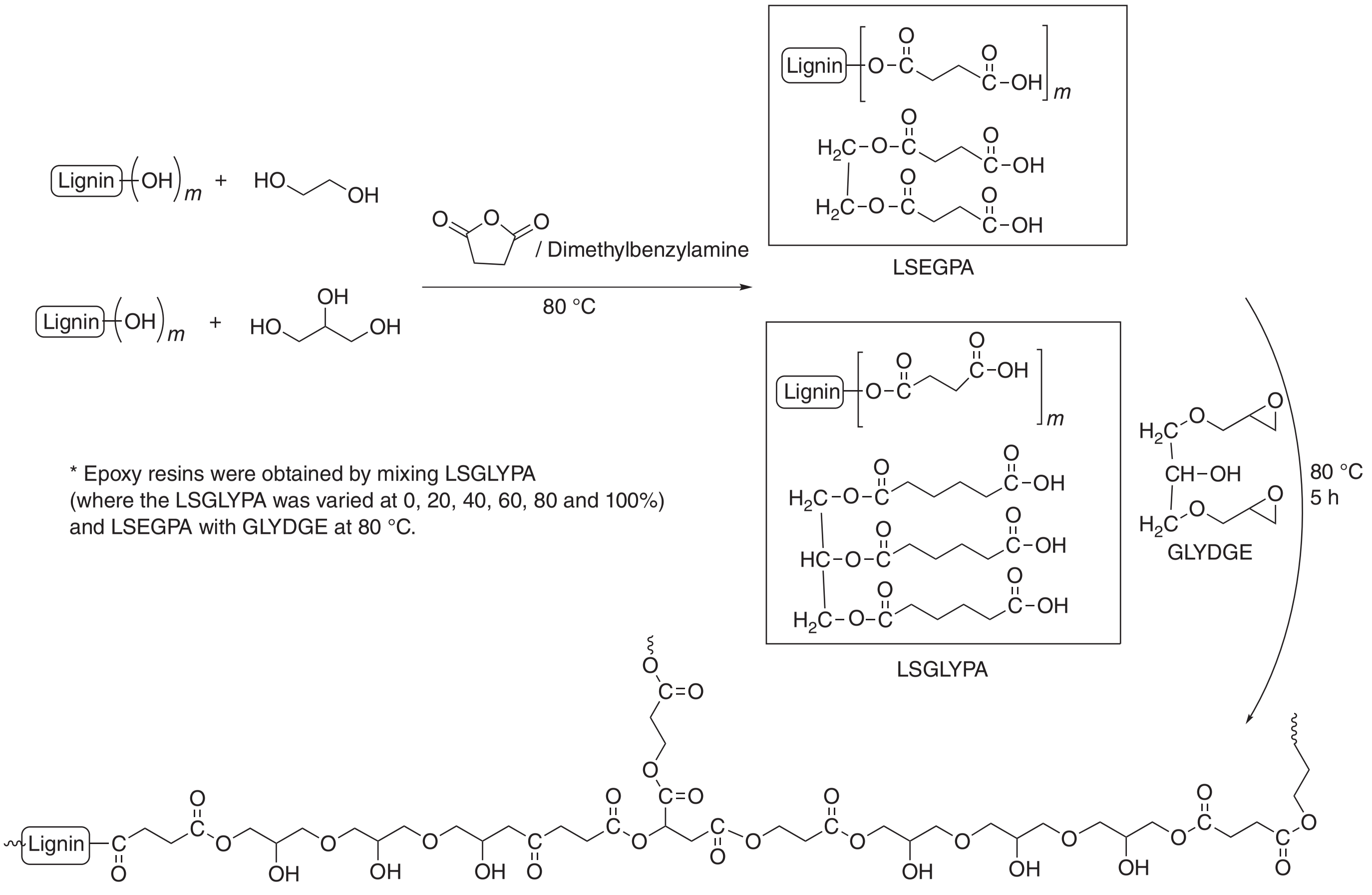
The glass transition temperature of the cross-linked epoxy resins increases with increasing LSGLYPA and GLYDGE contents. The increase of T_g for the product of the first synthesis is due to the increase in cross-linking density. In turn, for the second sample, an increase in the GLYDGE content increases T_g of the cured epoxy resins (hydrogen bonding became the dominant factor).

Vanillin can be converted into the diamine derivatives (Figure 1.62) [148].

Starting from diglycidyl ethers of 2-methoxyhydroquinone and vanillyl alcohol through an epoxy ring opening with ammonia, it is possible to obtain two primary amines, which could be applied as epoxy resin cross-linking agents. Because of β-hydroxyl groups present in the molecules of diamines, they exhibit the autocatalytic effect on the epoxy–amine reactions. These new β-hydroxylamines can be used for cross-linking of diglycidyl ether of methoxyhydroquinone and diglycidyl ether of vanillyl alcohol giving fully bio-based epoxy systems with good thermo-mechanical properties and high thermal stability.

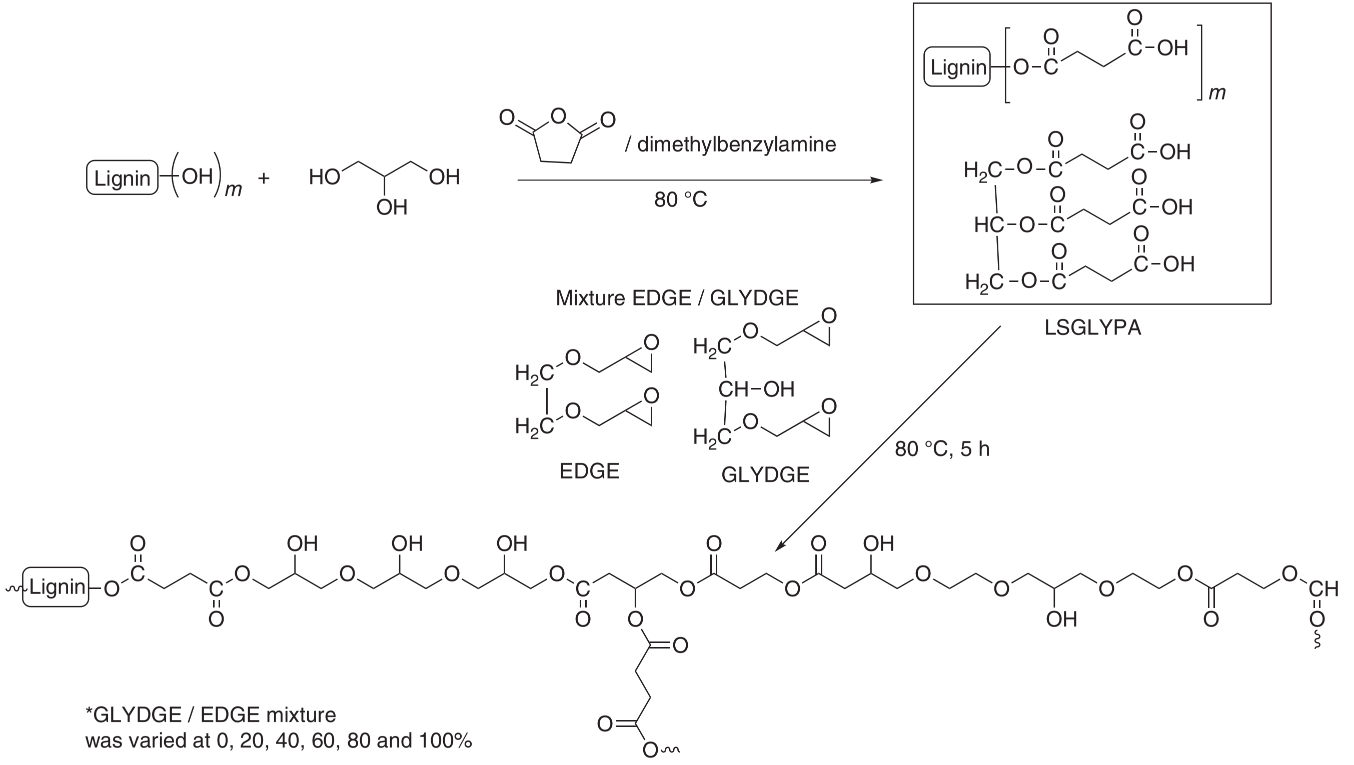
Cardanol derivatives are classified as the phenolic curing agents that are cross-linked with epoxy groups via the phenolic hydroxyl group. Novolac resins (Nov-I and Nov-II), containing an amount of unreacted cardanol of 35 and 20 wt%, respectively, are synthesized by the condensation reaction of cardanol and paraformaldehyde using oxalic acid as a catalyst (Figure 1.63) [149].

The cardanol-based novolacs might be used as curing agents of commercial (the diglycidyl ether of bisphenol A) epoxy resin in the presence of 2-ethyl-4-methyl-imidazole as a catalyst. The higher cross-linking density is observed with higher amounts of epoxy resin. Moreover, the resin cured with Nov-II is characterized by higher T_g and better mechanical properties than Nov-I-resin. On the other hand, because of the higher molecular weight and lower unreacted cardanol content, the similar thermal degradation properties are observed for both tested materials.



* Epoxy resins were obtained by mixing LSGLYPA
(where the LSGLYPA was varied at 0, 20, 40, 60, 80 and 100%)
and LSEGPA with GLYDGE at 80 °C.

Figure 1.60 Scheme of preparation cross-linked epoxy resin.



*GLYDGE / EDGE mixture
was varied at 0, 20, 40, 60, 80 and 100%

Figure 1.61 Scheme of epoxy resin by cross-linking LSGLYPA with a mixture of EGDGE/GLYDGE.

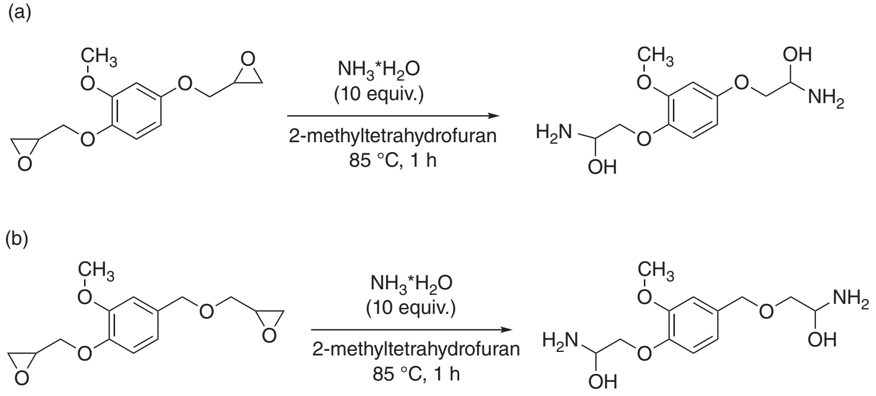


Figure 1.62 Synthesis of dihydroxyaminopropane of 2-methoxyhydroquinone (a) and (b) vanillyl alcohol.

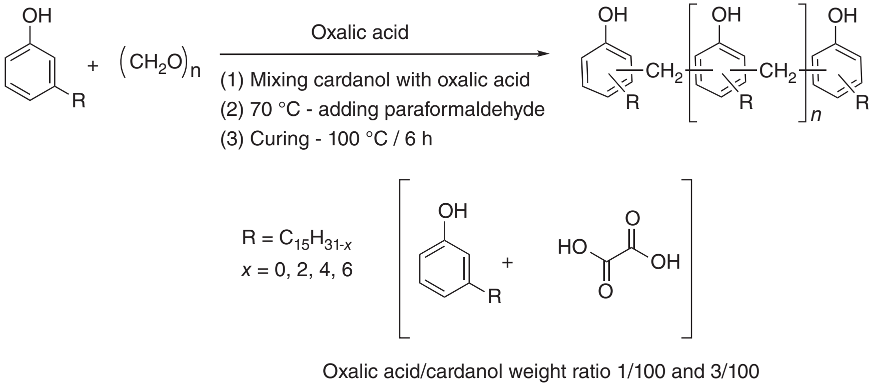


Figure 1.63 Synthesis of the cardanol-based novolacs.

The interesting cross-linking agent is possible to obtain as the diamine derivative of isosorbide (Figure 1.64) and it could be used for curing of diglycidyl ether of isosorbide giving the completely bio-based epoxy system [150].

The diamine derivative of isosorbide is obtained using microwave assistant thiol-ene coupling reaction in the aqueous media and with the water-soluble initiator $(NH_4)_2S_2O_8$, as the alternative to AIBN. The cured isosorbide-based resin has good shape fixity, good shape recovery, and satisfied thermal stability. This fully bio-based resin shows great potential to be used as a candidate for shape memory material. Another synthetic method for obtaining the diamine derivative of isosorbide is the reaction of cyanoethylation of isosorbide, followed by the hydrogenation of di-cyanoethylated product (Figure 1.65) [151].

Terpene derivatives might also be applied as bio-based curing agents for epoxy resins. For example, a novel terpene-based curing agent prepared as an adduct of myrcene, monoterpene containing three double bonds including conjugated diene, and maleic anhydride (MMY) is used to cure bisphenol A-based epoxy resin [152]. The obtained cured material is characterized by a tensile strength

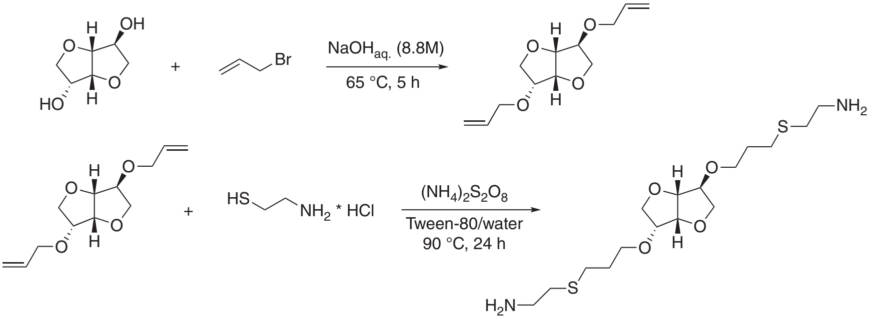


Figure 1.64 Synthesis of the isosorbide-based cross-linking agent.

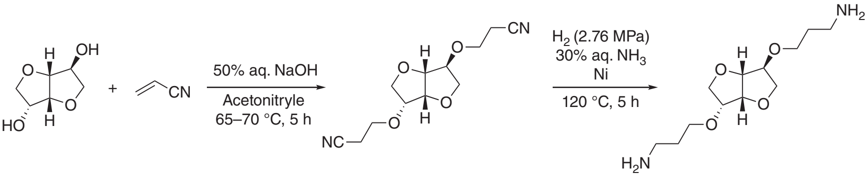


Figure 1.65 Synthesis of the isosorbide-based cross-linking agent via cyanoethylation step.

Table 1.7 Properties of epoxy resin networks cured with bio-based curing agents.

Cured samples	T_g (°C)	E at $T_{g+30°C}$ (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
MMY100	61.59	19.06	48.74	7.5	8.55
MMY75/CMMY25	58.03	19.00	42.11	6.5	13.87
MMY50/CMMY50	54.03	4.18	35.55	6.6	17.29
MMY25/CMMY75	45.09	2.72	11.11	259.4	62.51
CMMY100	15.14	1.11	0.43	565.8	Unbroken

of 48.74 MPa and a storage modulus of 19.06 MPa, but a poor impact property of 8.55 kJ/m^2 and a very low elongation at break (7.54%). Improvement of properties of cured bio-based epoxy resins is performed by application of mixture (mixed by weight ratios of 100/0, 75/25, 50/50, 25/75, and 0/100, respectively) of two curing agents: MMY and castor oil-modified adduct of myrcene and maleic anhydride (CMMY) (Figure 1.66).

Based on the obtained results (Table 1.7), with the increase of CMMY weight ratio, the tensile strength and T_g of the cross-linked resin decreases, but the elongation at break and the impact strength increase.

As can be seen from the examples presented above, it is possible to obtain not only epoxy resins from raw materials of natural origin but also cross-linking agents for them. Interestingly, it is also possible to synthesize completely bio-derived epoxy systems. Both the epoxy resins based on bisphenol A, as well

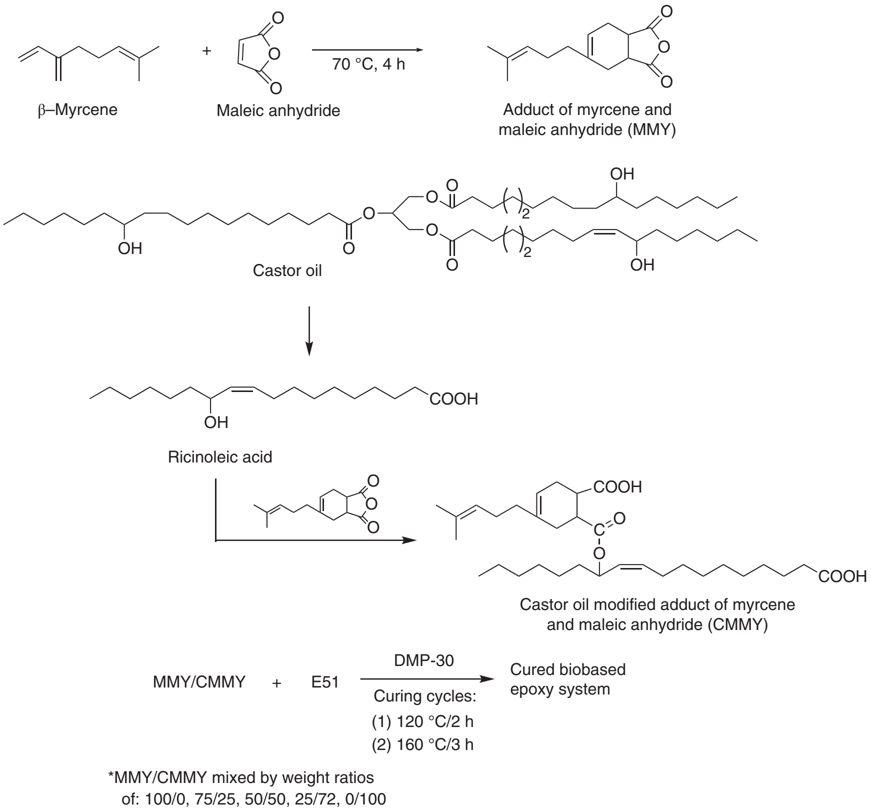


Figure 1.66 Synthesis of bio-based epoxy curing agent derived from myrcene and castor oil.

as cross-linked with curing agents on the basis of raw materials of natural origin, and the fully epoxy biosystems are characterized by very good final properties.

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